Quantum Well Thermoelectrics and Waste Heat Recovery

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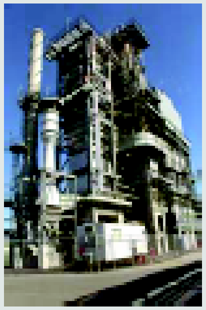
National Waste Energy Recovery

Magnitude of the Opportunity – Why Are We Interested?

- 60-70% of Energy in Most of Today's Processes Lost
- Transportation Sector
  - Light-Duty Passenger + Light-Duty Vans/Trucks (SUVs) Vehicles
    - 2002 – 129.8 Billion Gallons of Gasoline; 2004 – 135 Billion Gallons of Gasoline
    - Nationally Energy Equivalent of ~34-41 Billion Gallons of Gasoline/Yr Exhausted Down the Tail Pipe (~ 4.5 Quads)
    - Nationally Energy Equivalent of ~41-51 Billion Gallons of Gasoline/Yr Rejected in Coolant System (~ 5.5 Quads)

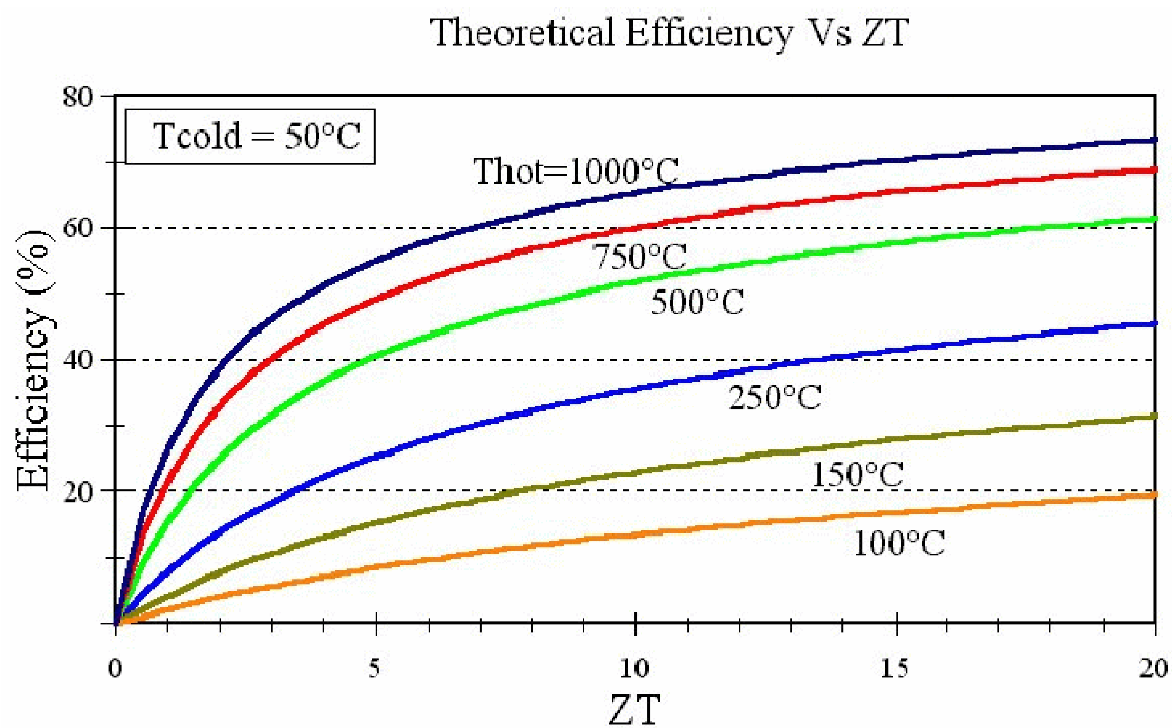
  - Heavy-Duty Vehicles
    - 75 – 240 kW of Waste Energy From Typical Diesel Engine
    - 2002 – 29.8 Billion Gallons of Diesel; 2004 – 32 Billion Gallons of Diesel
    - Nationally Energy Equivalent of 11 Billion Gallons of Diesel/Yr Exhausted Down The Tail Pipe (~1.45 Quads)
    - Nationally Energy Equivalent of 8 Billion Gallons of Diesel/Yr Rejected in Coolant System (~1 Quad)



- Industrial Process Sector
  - 10 Quads of Waste Energy Flows in Industrial Processes
    - Aluminum
    - Glass
    - Petroleum
    - Chemical
  - 1.8 Quads Recoverable

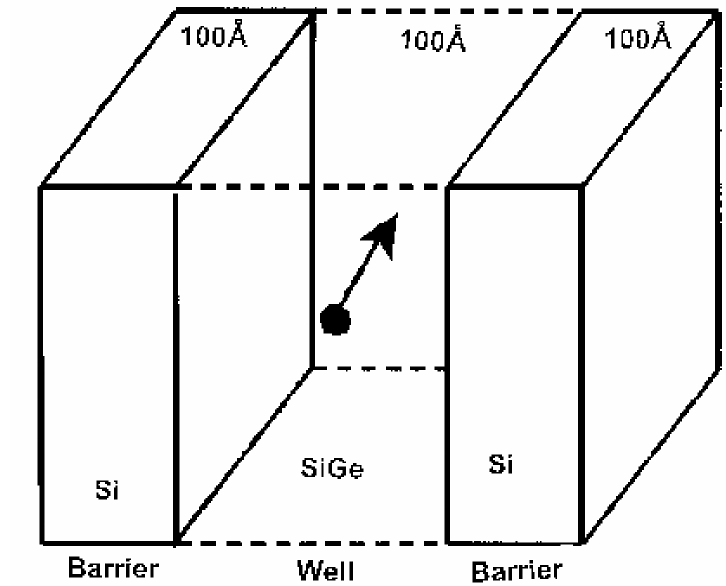
Thermoelectric Efficiency

$$Efficiency = \frac{T_H - T_C}{T_H} \; x \; \frac{M - 1}{M + \frac{T_C}{T_H}} \qquad M = \sqrt{1 + \frac{1}{2}\,\overline{Z}\,(T_C + T_H\}}$$



Two-Dimensional Quantum Well TE

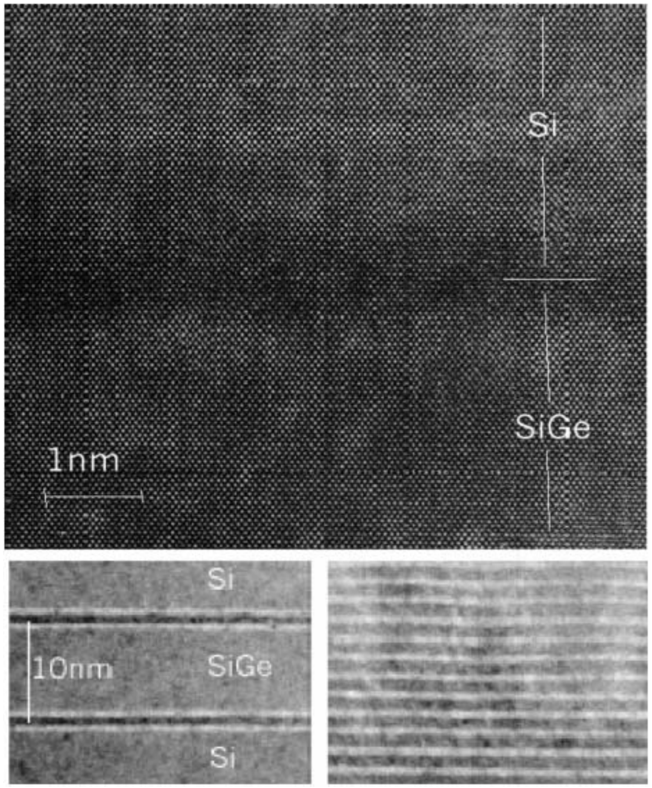
- Active layer sandwiched between materials with band offset to form a barrier for the charge carriers
- Increased Seebeck coefficient (α) due to an increase in the density of states
- Significant reduction on resistivity (ρ) due to quantum confinement of carriers
- Significant reduction on thermal conductivity (κ) due to strained lattice and other factors
- Quantum Well (QW) effects become significant at a layer thickness of <200Å

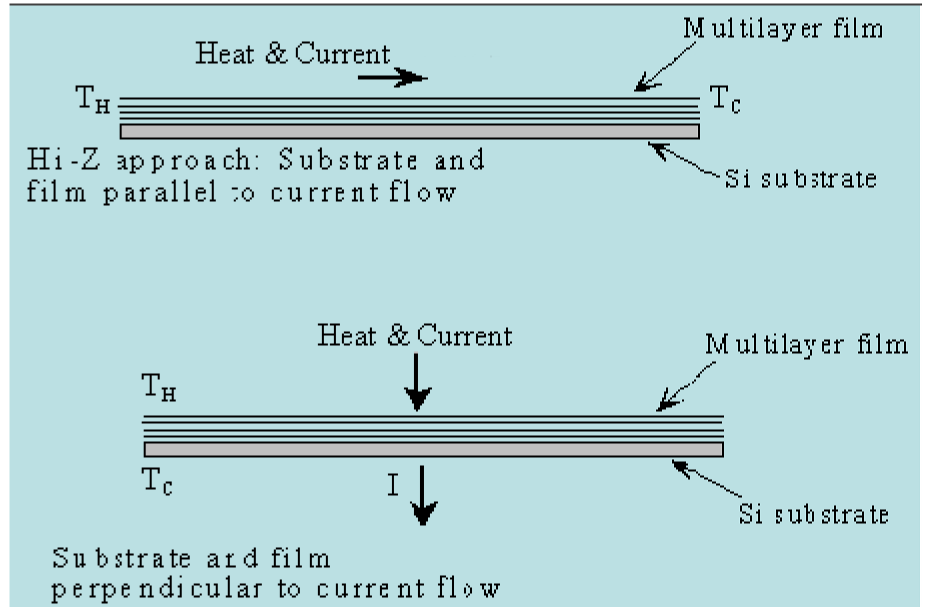


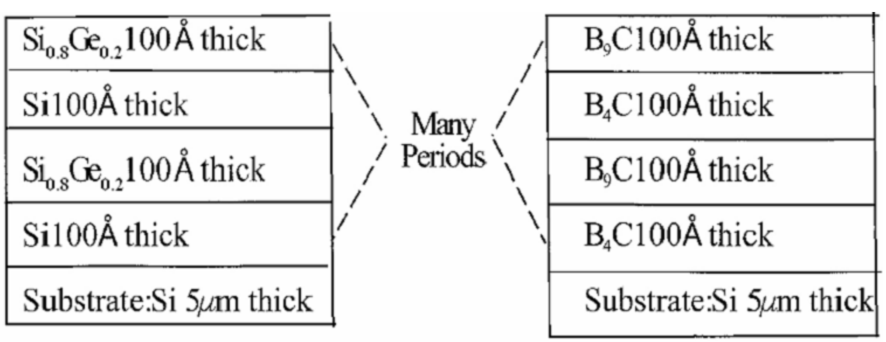
$Z = \alpha^2/\rho\cdot\kappa$

$ZT = (\alpha^2/\rho\cdot\kappa)T$

QW Orientation





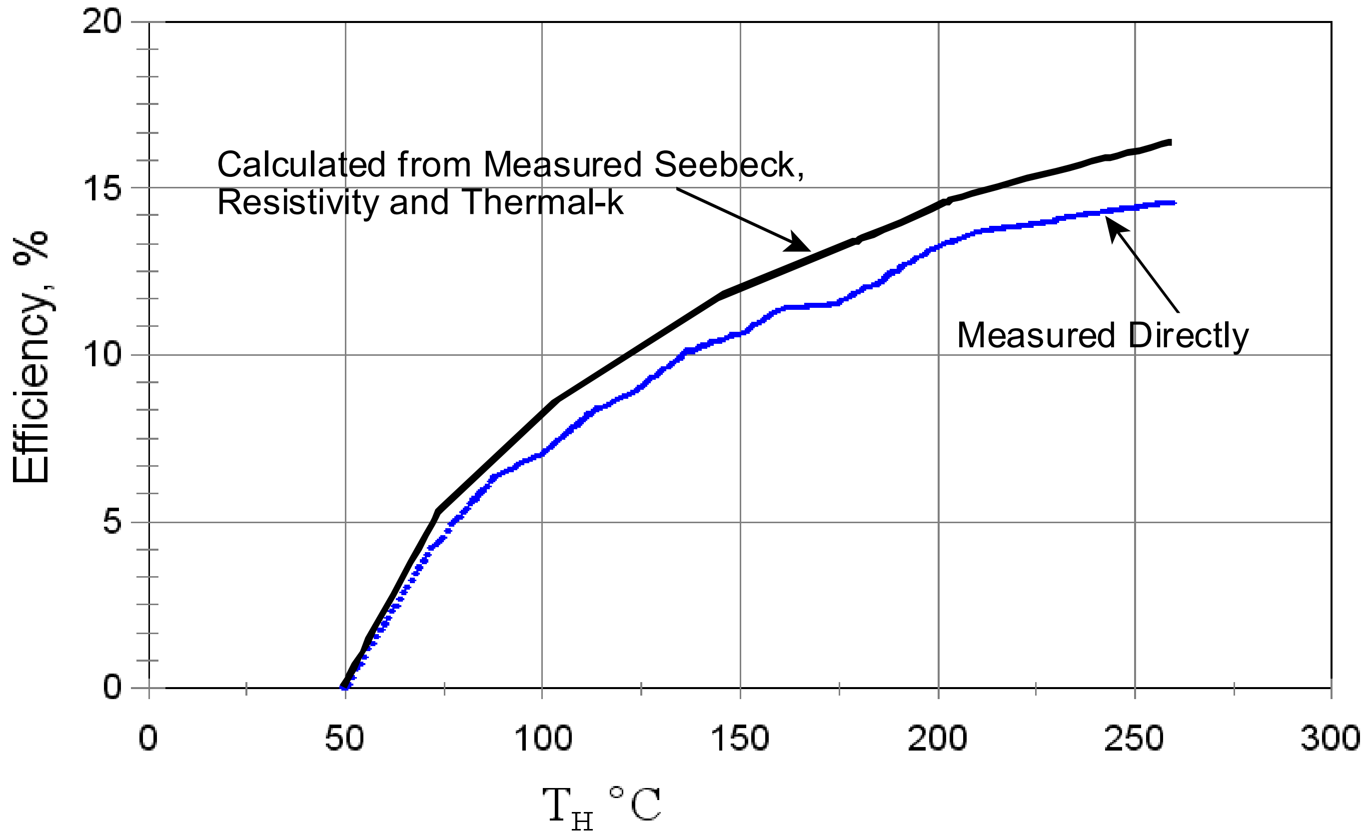


Criteria/Components for Developing QW Films

1. QW films
   - Compositions defined: N and P Si/SiGe, P type B_4C/B_9C and N type Si/SiC
   - Deposition parameters established with sputtering
   - Third party verification of QW films performed and continuing
2. Substrate
   - Need low thermal κ materials at low cost and can be readily coated with QW films
3. Joining techniques needed for fabricating couples that will operate at various T_H up to 1000☜C
4. Life testing of materials and couples
   - Isothermal
   - Gradient
5. Fabricate and evaluate modules
6. Continue cost analysis as fabrication techniques evolve

QW Couple Efficiency *Vs* Temperature

11 μm thick P type B_9C/B_4C and N type Si/SiGe on 5 μm thick Si



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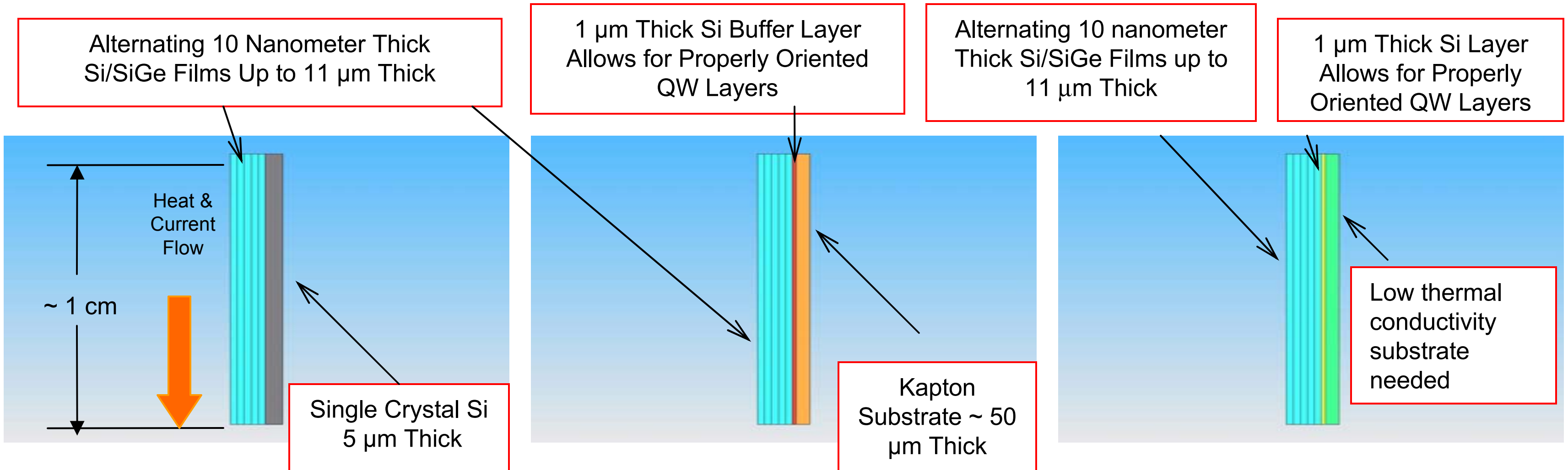
Comparison of Initial Concept and Pursued Concepts



Initial Concept and Demonstration

- Yielded 14% efficiency at a T_H of 250°C, T_C 50°C when used as N leg and P leg was B_4C/B_9C
- Single crystal Si substrate has too high a thermal conductivity
- Parasitic heat loss >50% because of single crystal Si
- Biggest gain to be made is to reduce the thermal κ of the substrate

Proposed for < 300°C Operation

- Kapton is flexible, and lowest thermal κ of any substrate
- Si buffer layer is deposited to allow the Si/SiGe to achieve proper orientation
- Parasitic heat losses estimated at ~5%
- Results dependent on Kapton surface finish

Proposed for High Temperature Applications

- Alternate substrates are poly-crystalline Si, glass and SiGe
- Polycrystalline Si or SiGe thermal κ 10X lower than single crystal Si

Coating Criteria

- QW materials must be alternately deposited at 10 nanometer intervals on some substrate.
- A lower thermal conductivity substrate is used to deposit the QWs since the heat will flow in parallel through the QW films and the substrate.
- The ratio of QW thickness to substrate's thickness needs to be maximized to minimize heat flow.
- Since the sputtering of QW films is slow and expensive, the incentive is to minimize the number of QW films required, which in turn requires the substrate thickness to be minimized.

Projected Efficiency of Quantum Wells With Low Thermal Conductivity Substrates such as Kapton

	Measured Seebeck Coefficient α $\mu V/K$	Measured Electrical Resistivity ρ $m\Omega$-cm	Power Factor α^2/ρ $\mu W/cm$☜C	Average ZT[1]	Projected[1] Efficiency 50-250☜C T_C - T_H %	Projected[1] Efficiency 50-600☜C T_C - T_H %
Typical former QW sample at room temperature	1100	1.0	1,210	~3	13	23
Recent QW sample material •Measurements observed by UCSD and NIST	1200 1200	0.04[2] 0.8[3]	36,000 1,800	~4.5	17	25[4]
Current Bi_2Te_3 Bulk Alloy	220	1.1	44	<1	5	Properties degrade >300☜C

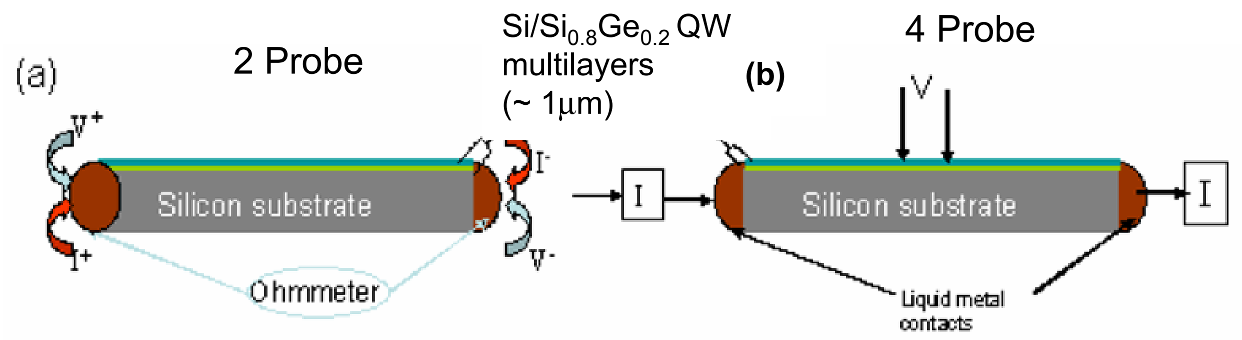
[1] α and ρ measurements near room temperature; κ is published data

[2] 4-probe resistivity measurement

[3] 2-probe resistivity measurement

[4] For Si/SiGe not B_4C/B_9C and Si/SiC

Schematic of the Measurement Setups for Obtaining the Restivity (R) of the Si/SiGe Multilayer on Si Substrates

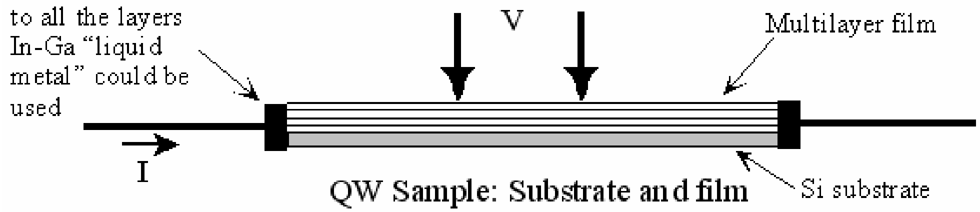


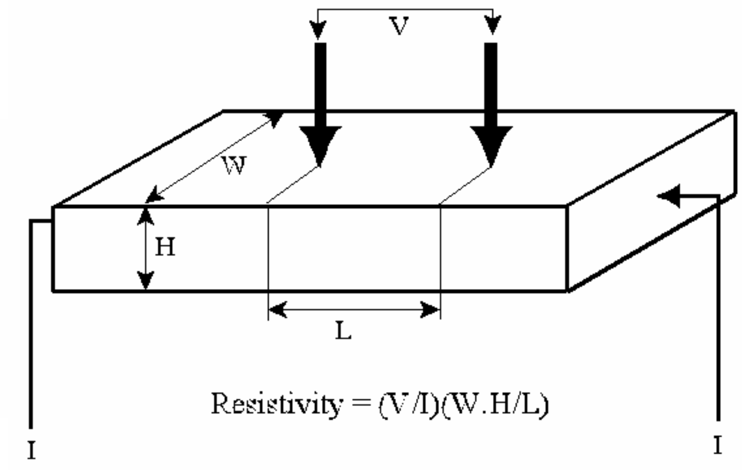
(a)two-terminal Ohmmeter (Tegam, Inc.) probes and,

(b)A four probe arrangements, where the current is sent through the liquid metal contacts at the ends while the voltage is measured along the sample with two more probes. Note: typical specimen is grown to 8-10 µm of Si/SiGe multilayers. However, test specimen had 1 µm Si/SiGe

The resistivity parallel to the layers (ρ||) is then calculated from measured resistance (R) through the sample geometry. The lateral dimensions of the sample are 1.2 cm x 0.5 cm, and the thickness of the Si/SiGe multilayer are ~1 µm (the substrate is ~500 µm thick).

4-Probe Resistivity





• The resistivity of the QW samples is measured by inputting the current at the ends and measuring the voltage drop in the center

• With Si substrates, critical to the measurement is contacting all the films and substrates with liquid InGa

•With Kapton substrates we are unable to use InGa. Mo is used to obtain low resistance contacts

Resistivity Cont.

The measured resistance R_{total}, consists of the resistance of the film, R_{films}, and the resistance of the substrate, $R_{substrate}$,

$$\frac{1}{R_{total}} = \frac{1}{R_{substrate}} + \frac{1}{R_{film}} \qquad (1)$$

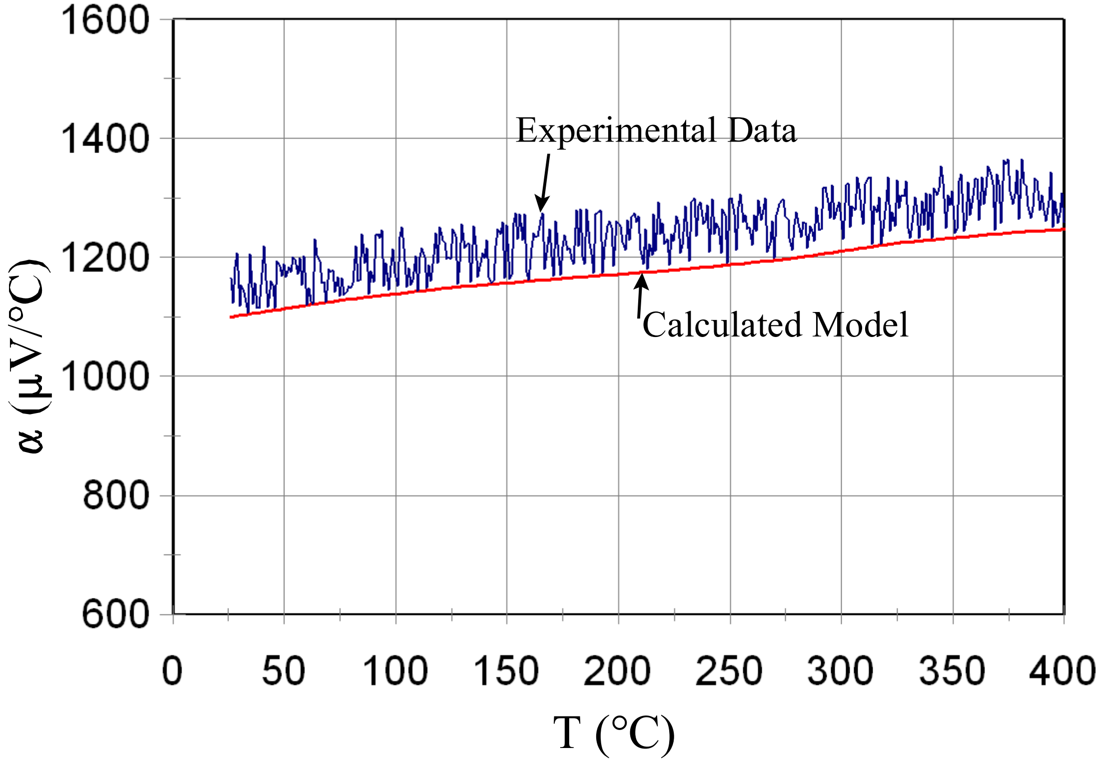
By making independent measurements of the substrate resistance, the film resistance can be calculated from the measured value,

$$R_{film} = \frac{1}{\frac{1}{R_{total}} - \frac{1}{R_{substrate}}} \qquad (2)$$

Given the dimensions of the film the actual conductivity of the QW sample can then be calculated directly,

$$\sigma_{films} = \frac{1}{\rho_{films}} = \left(\frac{L}{WH}\right)\frac{1}{R_{films}} \qquad (3)$$

Calculated *vs* Experimental Seebeck Coefficient *vs* Temperature for QW Films



The calculated model closely matches the experimental data. This excellent match between the analytical and experimental data underscores the model's viability for understanding the α behavior.

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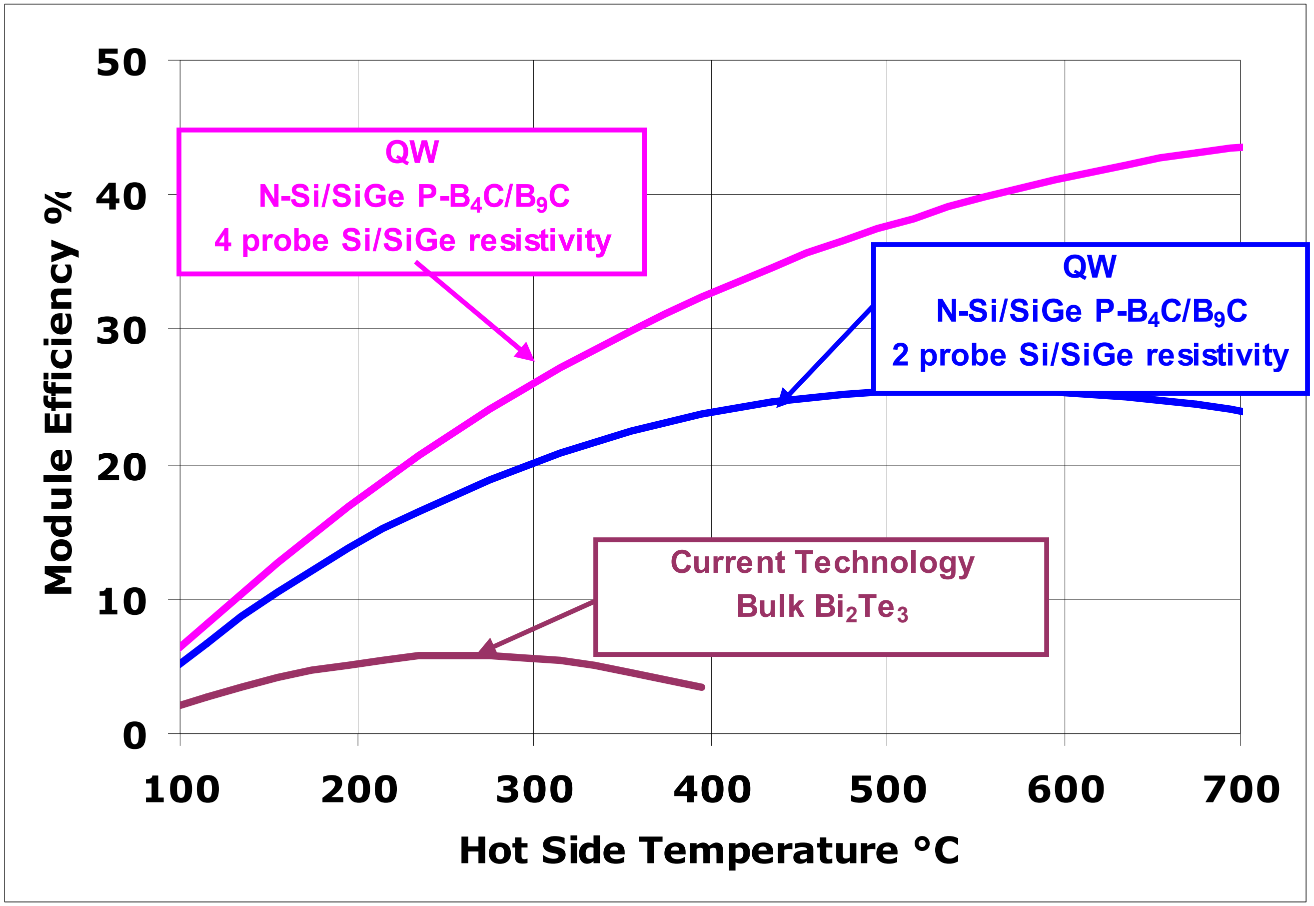
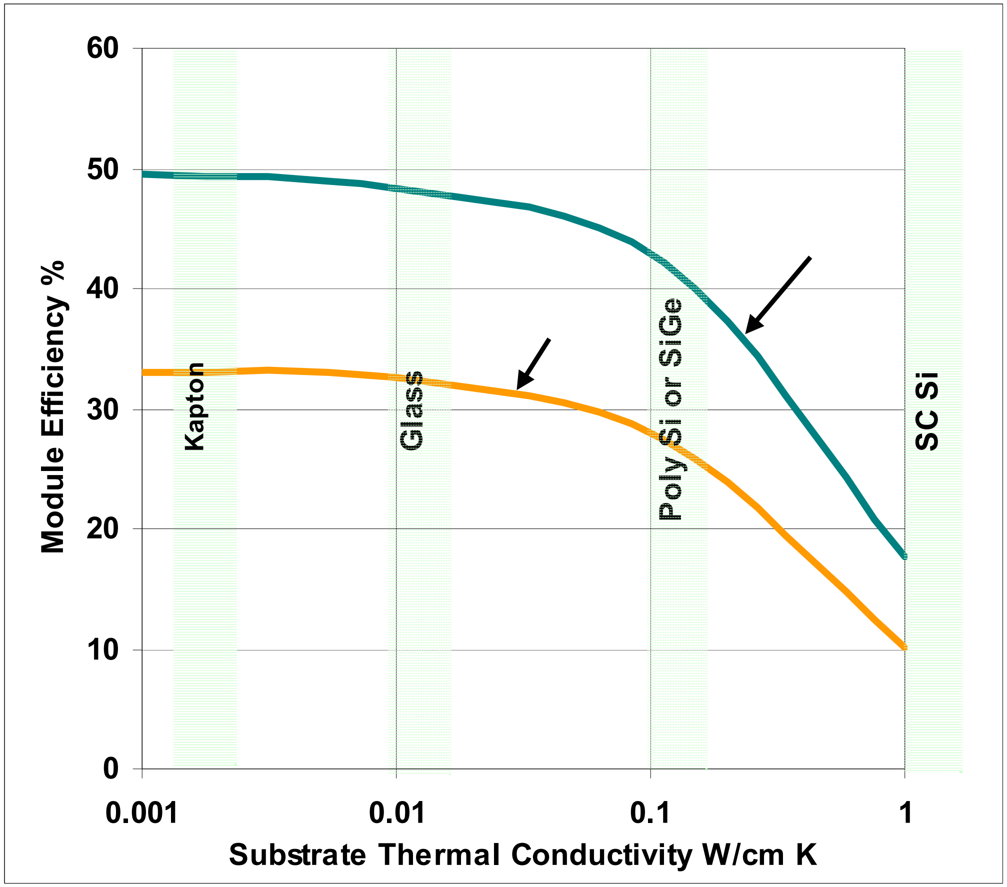
Potential Increase in Maximum Efficiency for a Quantum Well Module Compared to Bi_2Te_3



Potential Si/SiGe QW TE Module Efficiency with Various Substrates

- Efficiency is strongly dependent on substrate thermal conductivity
- Best QW properties obtained on Single Crystal (SC) Si
- Predicted QW efficiencies for 0.051 mm (0.002 in.) substrate using recent NIST (3/07) and UCSD (12/06) measured QW properties



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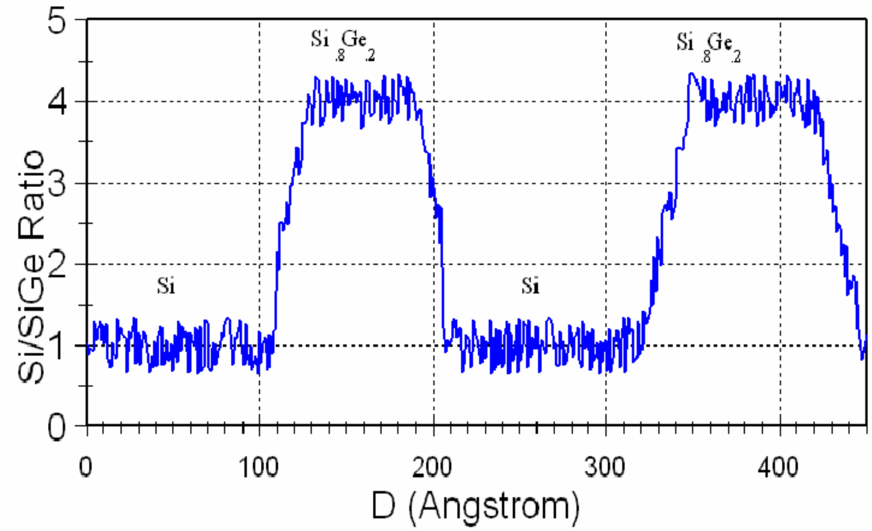
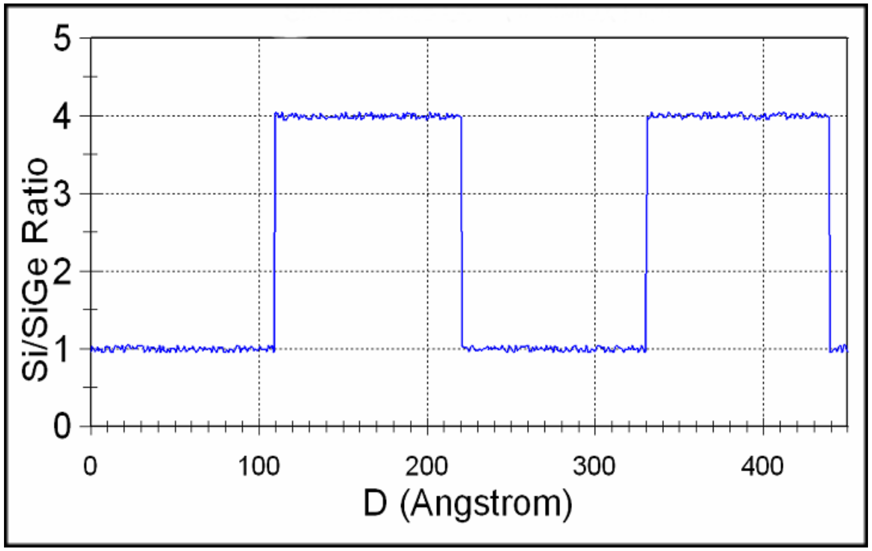
Auger Electron Spectroscopy (AES) Comparison

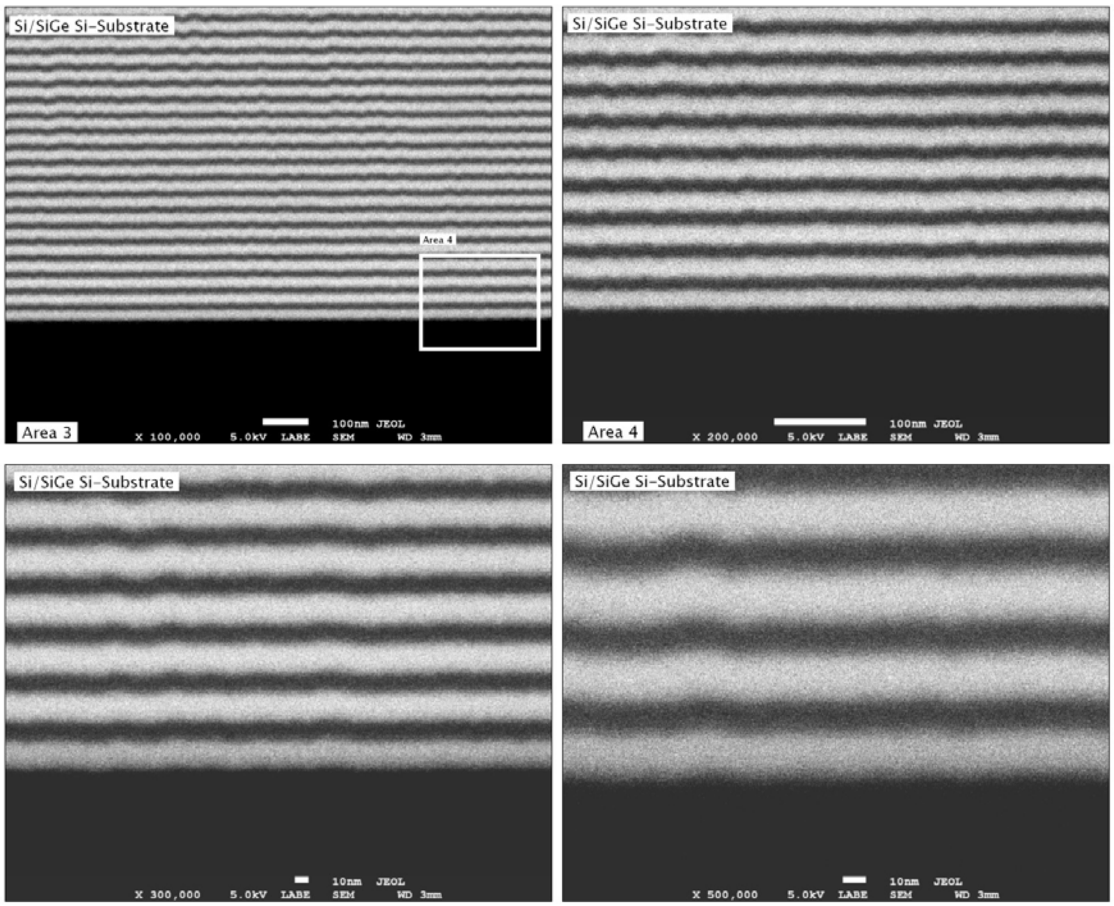




- QW Film on Kapton Substrate
- QW Film on Single Crystal Si Substrate

Si/SiGe Films on Cross-section

Films were sectioned and then viewed by SEM (scanning electron microscopy)



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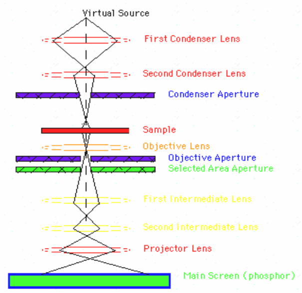
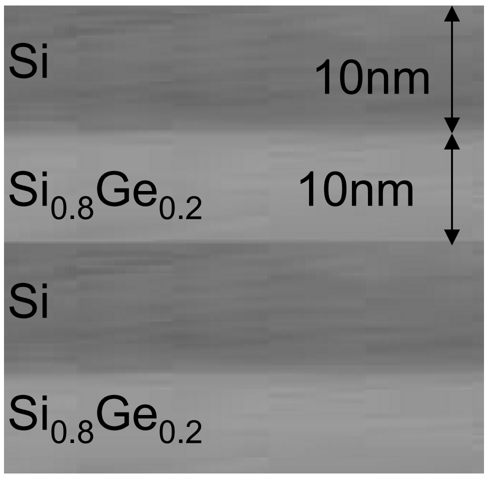
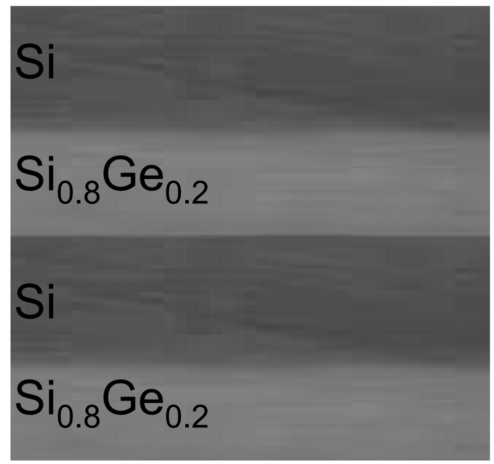


Transmission Electron Microscopy (TEM) of Aged QW Films

•TEM before aging



•TEM after 1000Hr aging near 300°C of couple @ T_{hot}300 -T_{cold}50°C

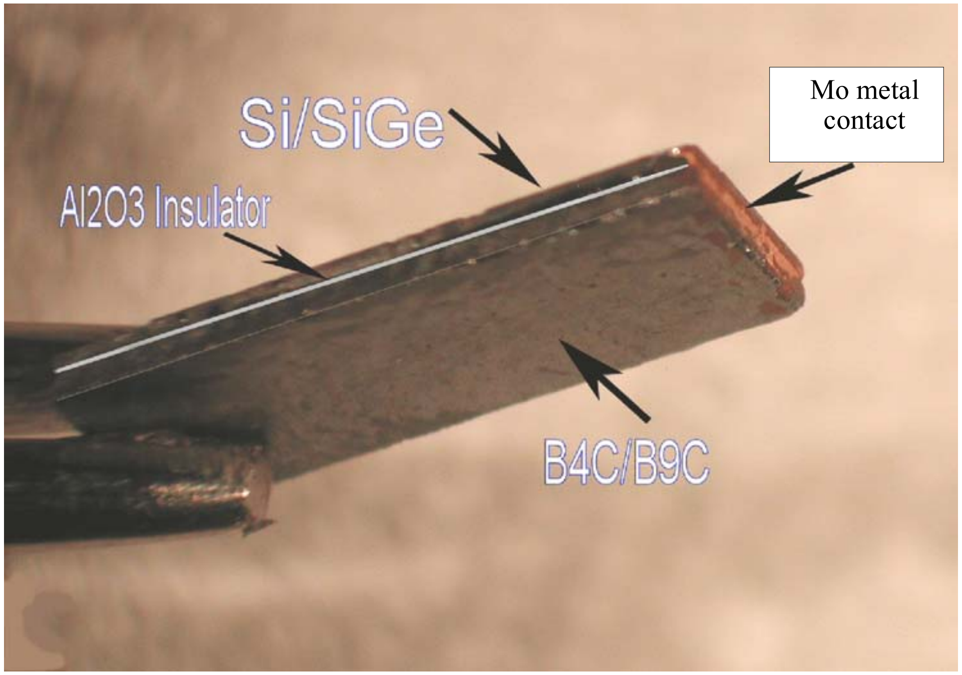


- Each layer is ~100Å thick

•The boundaries between each layer are as sharp as the as fabricated films indicating no diffusion is occurring and films do not break up

•TEM, X-ray and thermoelectric properties measurements confirm QW thermal stability

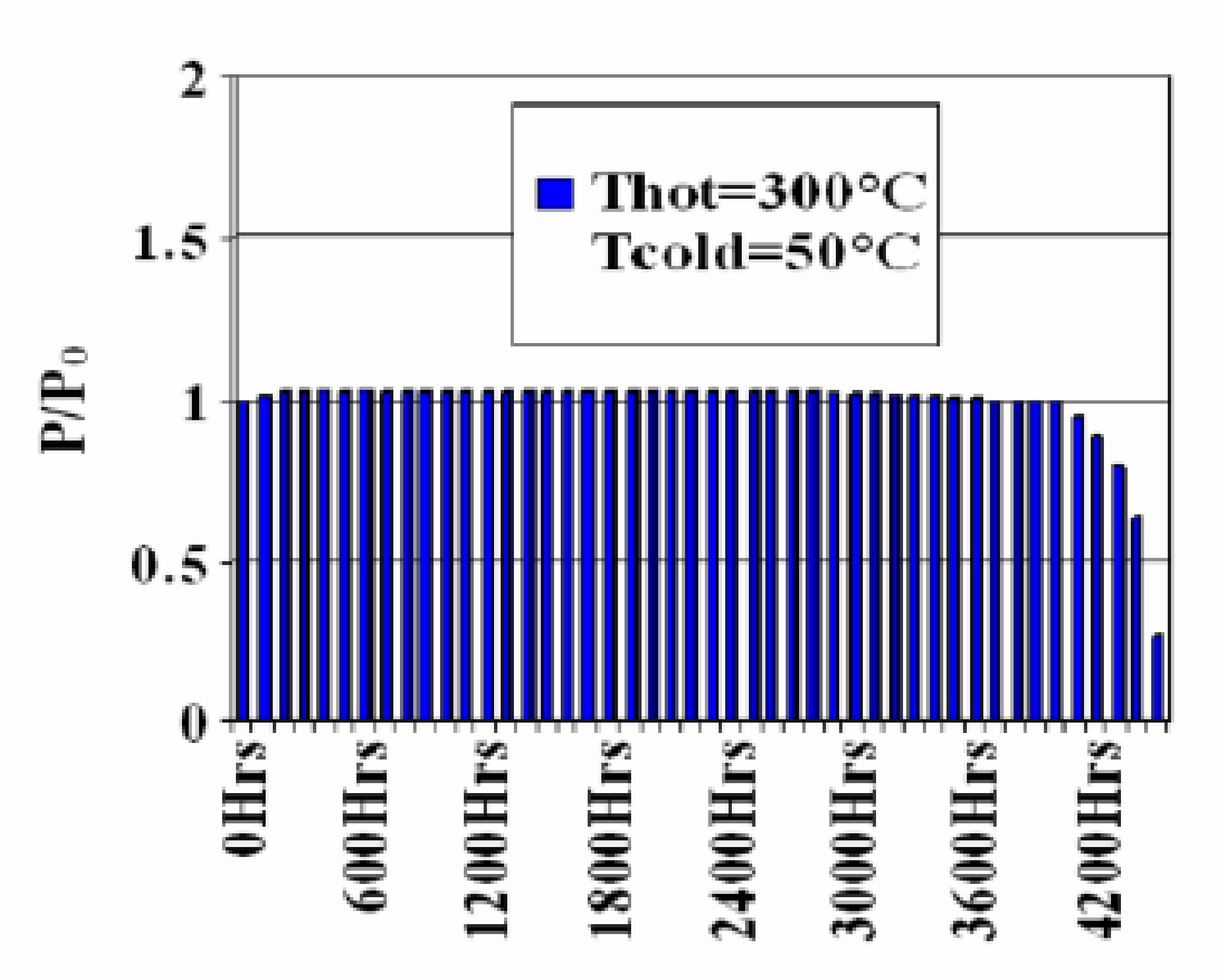
Molybdenum Contacted QW Couple



Thermoelectric properties of QW couple with Mo contact compared to calculated values

Room temperature properties	Measured	Calculated
Couple Resistance	1.23 kΩ	1.25 kΩ
Couple Voltage Output @ $\Delta T \sim 5^{\circ}C$	9.56 mV	9.60 mV

Life Test Data



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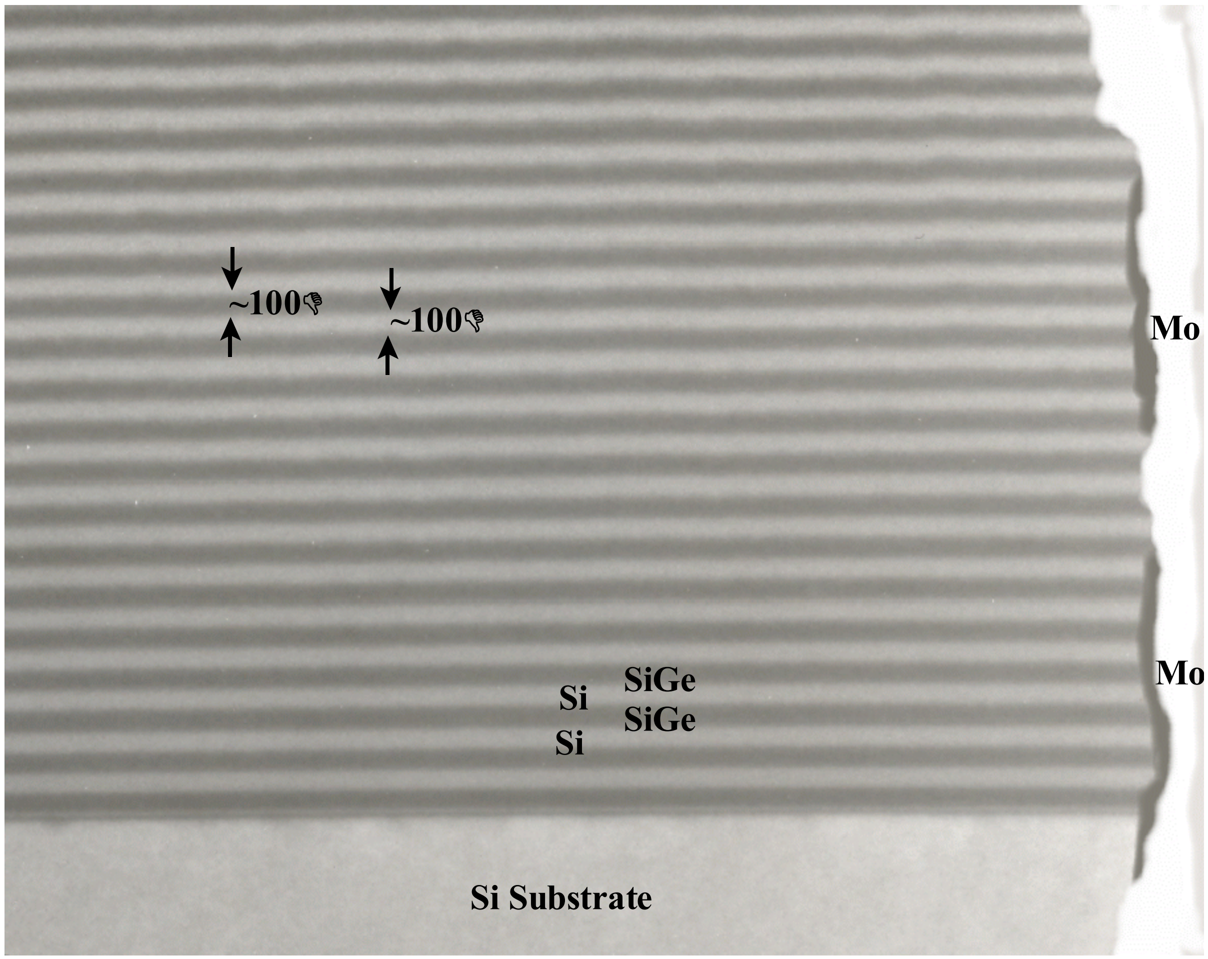
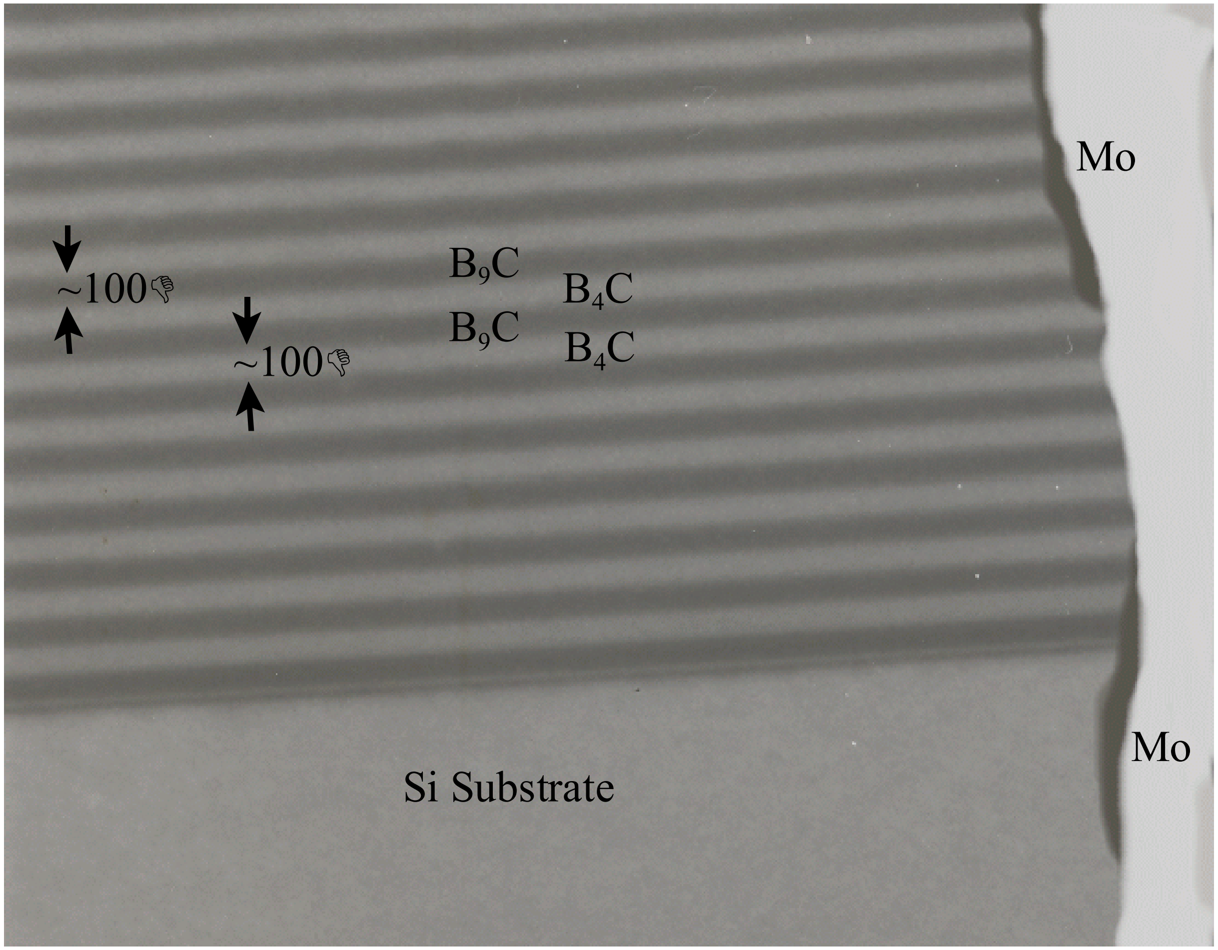
150 kX SEM of Si/SiGe Leg of the ~4000 Hours Aged Couple

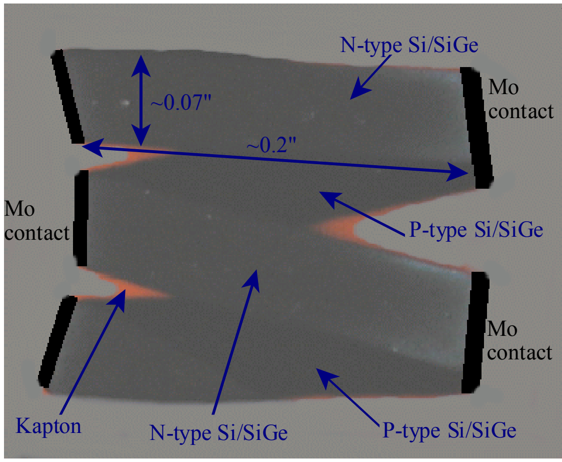


150 kX SEM of B_4C/B_9C Leg of ~4000 Hours Aged Couple

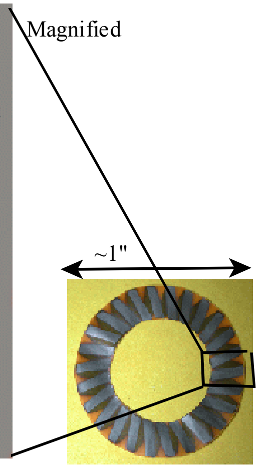


Si/SiGe Deposited on Kapton™ Substrate

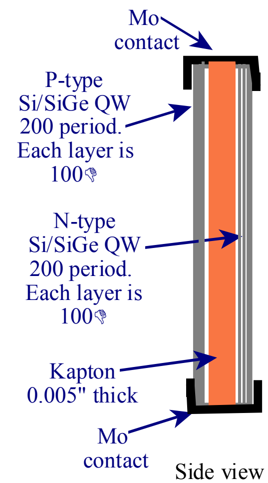
Fabrication Approach



Two couple device with N&P Si/SiGe QW on Kapton substrate



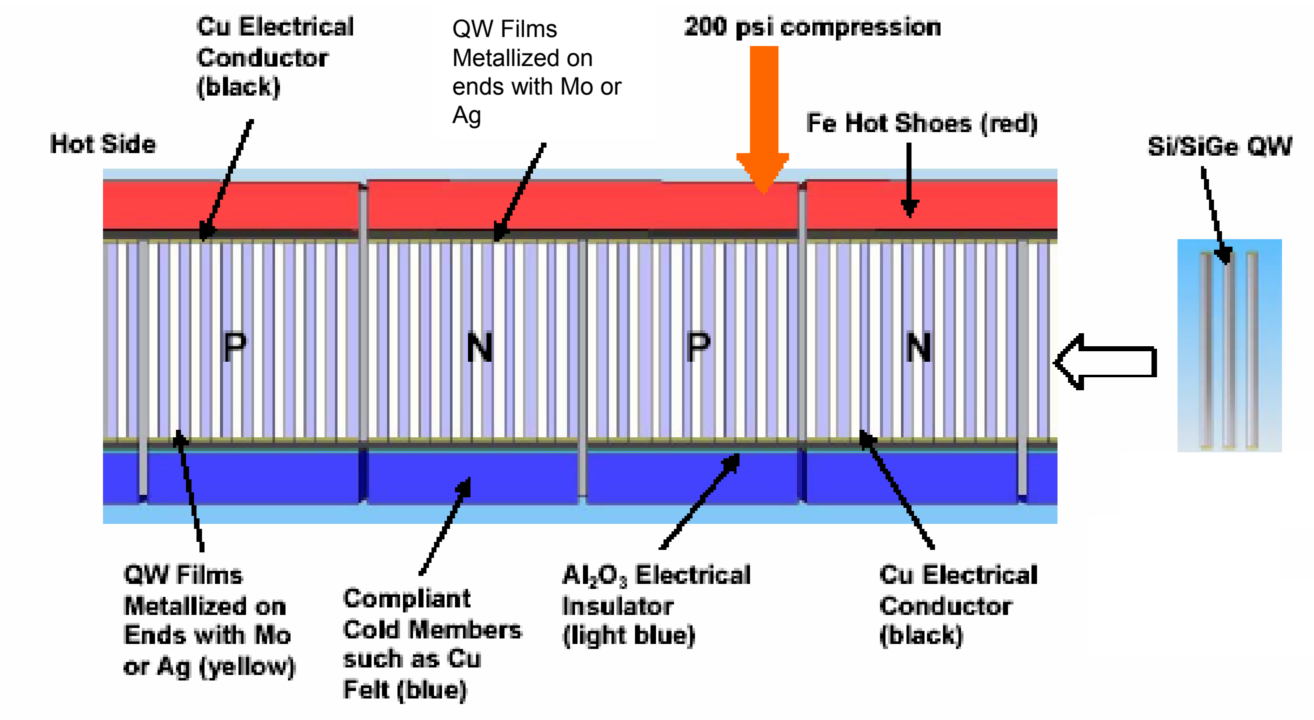
Complete 26 couple device



Results

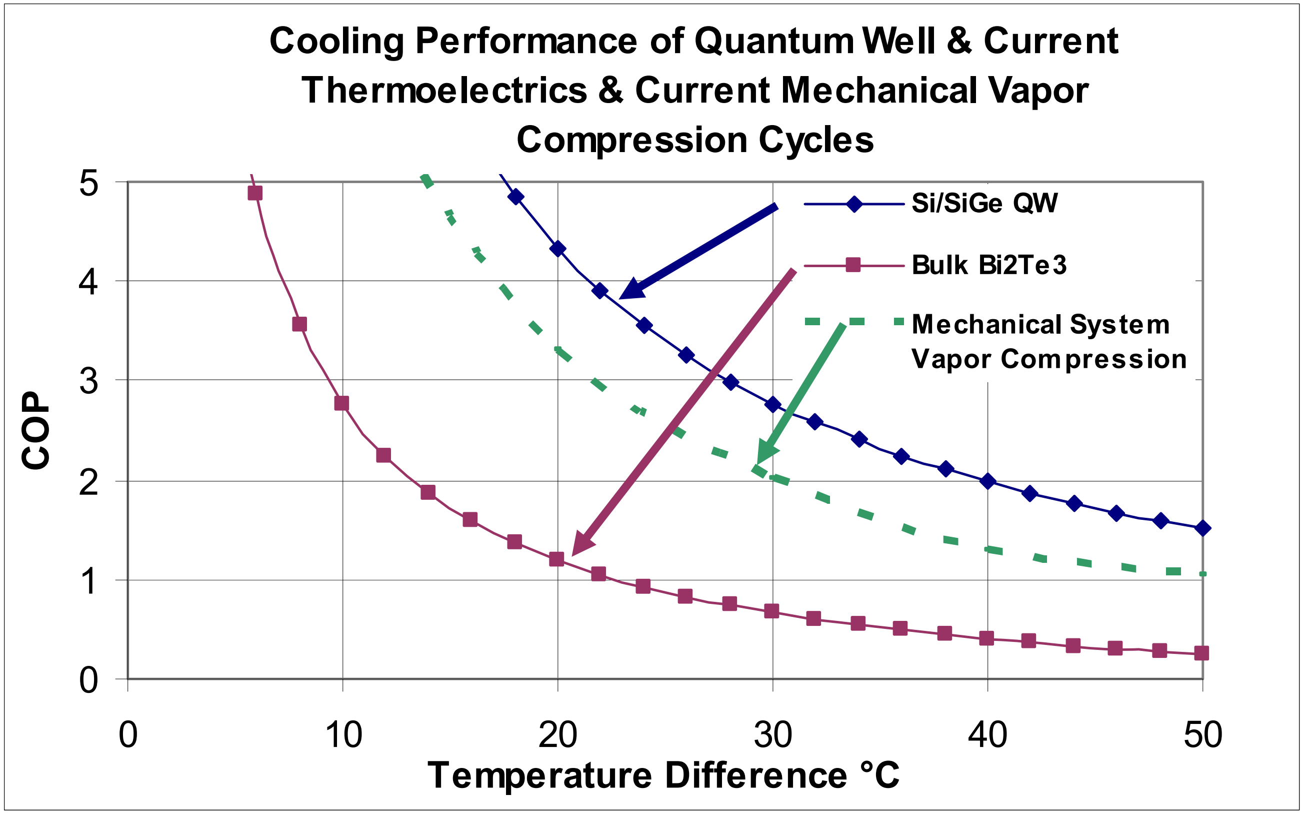
	Experimental		Calculated	
	2 Couples Measured at $\Delta T = 40°C$	Results 2 Couples Measurements Extrapolated to 26 Couples at $\Delta T = 40°C$	26 Couples at $\Delta T = 40°C$	
$T_{COLD} = 26°C$ $T_{HOT} = 66°C$			Quantum Wells Si/SiGe with ZT ~ 3.0	Bulk $(Bi,Sb)_2(Se,Te)_3$ With ZT ~ 0.75
Voltage (V_{OC})	225 milli Volt	2.93 V	3V	0.5V
Power	0.371 milli Watt	4.82 milli Watt	5 milli Watt	1.5 mili Watt

Schematic Showing two N and P Couples in a Quantum Well Module



Each leg consists of ~100 layers of 11 μm Si/SiGe on 1 μm Si buffer layer on 50 μm Si substrate. The assembly is based on prior PbTe work where this design provides excellent thermal contact with compliant members and will allow a large number of thermal cycles for power and cooling modules.

SiGe Quantum Wells for Cooling Application



Quantum well thermoelectrics have large coefficient of performance that competes with mechanical vapor compression cycle.

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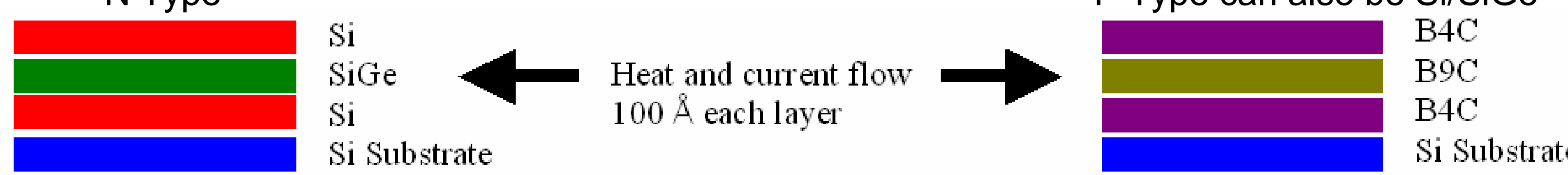
QW Thermoelectric Cost Estimation

- Raw materials
  - Si $37.20/kg
  - Ge $956.30/kg
  - B $94.15/kg
  - C $16.10/kg
- Sputtered 2μSi on 1 mil Kapton: $21.14/m^2 – In production today
- High volume cost for QW TE: ~0.30/Watt

Summary of Present Status

1. Alternating 100 Å (10 nm) thick layers of N type Si/SiGe and P type B_4C/B_9C deposited on 5 µm thick Si substrates

QW like behavior is observed "*in plane*"



- 14% efficiency measured at a T_H of 250°C and T_C of 50°C
- Recent data with a ZT of ~5 indicates higher efficiencies of >20% feasible at same T_H and T_C
- Goal is to achieve the Si/SiGe resistivities of 0.04 mΩ-cm with N and P couples.

2. Good thermal and thermoelectric stability exhibited thus far:
   - In isothermal testing at 600°C, 400 hours and 1000°C, 24 hours
   - In near constant power output of a N and P couple at T_H of 300°C and T_C of 50°C, 4000 hrs.
   - Hot side bond cracked at >4000 hours; N and P legs did not change in TE properties
3. Large area deposition:
   - Sputtered QW film onto 9 inch area
   - Major coating facility has teamed, has large scale production sputter facility
4. Identified QW film compositions, upgrading deposition parameters, begun couple fabrication.
5. Joining with Mo shows promise. Improved materials and techniques required.
6. Lower thermal conductivity substrates being pursued via several techniques. Kapton may also be suitable as a substrate
7. Projected Quantum well modules <$0.30/Watt

Conclusions

1. The Si/SiGe QWs are exhibiting very favorable Seebeck coefficient (α) and electrical resistivity (ρ). These data are much improved over any other bulk alloys.
2. The α and ρ data has been observed by two other individuals, one at UCSD (University of California San Diego) the other at NIST (National Institute of Standards and Technology). Other investigators welcome.
3. Large increases in thermoelectric conversion efficiency appear feasible from T_H's of 150☜C to 1000☜C.
4. With higher efficiencies large waste heat recovery markets become economical. Today they are marginal.
5. Hi-Z is pursuing the further fabrication and evaluation of QW materials, couples and modules to satisfy this much needed technology.