

Predicted Performance of Quantum Well Thermoelectrics for Power Generation

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Predictions of power output with quantum well films shows greater than 15% efficiency at a $\Delta T = 200^\circ\text{C}$ and greater than 30% efficiency for a $\Delta T = 400^\circ\text{C}$. Quantum well thermoelectrics provide significantly more power and efficiency than Hi-Z's current commercial Bi_2Te_3 alloys. Data and analysis show how performance (power, efficiency, voltage, *etc.*) depends on the quantum well film material and substrate material. A low thermal conductivity substrate reduces parasitic heat losses and increases efficiency; and also provides a design method to adjust for the operational environment. Hi-Z has measured the thermoelectric properties (α, ρ, κ) of N-type Si/SiGe and P-type $\text{B}_4\text{C}/\text{B}_9\text{C}$ on a 5 μm thick Si substrate from room temperature to 260°C and fabricated a couple demonstrating 14% efficiency at a temperature difference of 200°C . Based on this data, concept design features for quantum well modules and electrical generators are reviewed. Latest data on quantum well materials, mini-modules and efficiency are reviewed and implications presented for applications from milliwatts to many kilowatts

Nomenclature

α	=	Seebeck coefficient
ρ	=	Electrical resistivity
κ	=	Thermal conductivity
Si/SiGe	=	Quantum well thermoelectric films – N-type
$\text{B}_4\text{C}/\text{B}_9\text{C}$	=	Quantum well thermoelectric films – P-type
Bi_2Te_3	=	Bulk thermoelectric material
Z	=	Figure of Merit
μm	=	micrometer

I. Introduction

Hi-Z has developed, fabricated and tested new quantum well materials that offer 15-20% efficiency over operating temperatures between 250°C and 50°C . These improved materials are now evolving on presently funded DOE/DOD programs and will compete with traditional energy conversion cycles while providing solid state energy conversion.

Predictions of performance are presented herein for quantum well thermoelectrics for generation of electricity from readily available modest temperature (35°C) environmental sources and higher temperature ($\sim 250^\circ\text{C}$ - 500°C) industrial sources including vehicle exhaust, chemical plants, solid oxide fuel cells, incinerators and geothermal plants. Quantum well thermoelectrics are shown on to have broad applications from milliwatts to kilowatts.

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II. Construction and Arrangement of Quantum Well Films

A quantum well film is formed by alternating thin ($\sim 100\text{\AA}$) layers of two materials with differing electron band gaps such as Si and SiGe as shown in Fig. 1. With these QW materials a large (factor of ~ 3) increase in α and a reduction in κ and ρ was observed in the mid 1990s by Hi-Z and others [1,2,3,4]. These improvements resulted in a much improved figure of merit, Z , and therefore an improved conversion efficiency (η).

QW films can be used either in the direction of the deposited films or perpendicular to the direction of the films as discussed below and shown in Fig. 2. In either direction an improvement in Z usually occurs. However, Hi-Z prefers the in-plane use because (1) much higher Z s are achieved, since all three thermoelectric properties, α , ρ , and κ are improved to yield a large increase in the figures of merit, Z , and (2) it will be much easier to design and implement this approach in devices because the A/L ratio can be easily controlled for low or high heat fluxes, and (3) the perpendicular direction requires a very high A/L, which implies very high and undesirable heat fluxes.

- Si/SiGe: Multilayer Quantum Well film thermocouples
- P-type B_4C/B_9C : High temperature thermally stable multilayer Quantum Well films
- Si/SiC Quantum Well development underway to replace Si/SiGe for power (higher temperature) applications

Si _{0.8} Ge _{0.2} 100Å thick	Many Periods	B ₉ C 100 Å thick
Si 100Å thick		B ₄ C 100 Å thick
Si _{0.8} Ge _{0.2} 100Å thick		B ₉ C 100 Å thick
Si 100Å thick		B ₄ C 100 Å thick
Substrates: Si 5μm thick		Substrates: Si 5μm thick

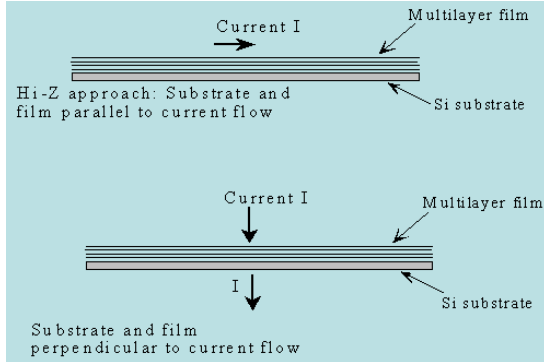


Figure 2. QW films can be used parallel or perpendicular to current flow. However, higher Z s are obtained in the parallel direction due to QW behavior. When used in the perpendicular direction, no QW behavior (enhancement) is obtained but the κ is lowered due to the many film interfaces.

Figure 1. Construction of quantum well films.

As shown in Fig. 3 multiple pieces of the planar $11\ \mu\text{m}$ thick QWs can be assembled and loaded into an eggcrate which forms a thermoelectric module. Each of these pieces are then in parallel with other pieces in each N or P leg in the eggcrate. The ends of the QW are metallized and this metal surface forms a pressure contact with the electrical conductors. This same concept was developed for PbTe alloy [5] and proved satisfactory for accommodating thermal stresses.

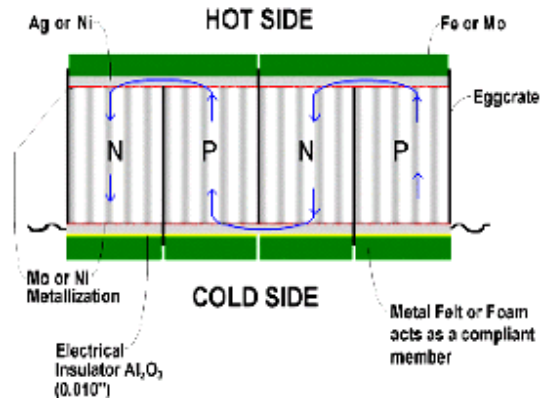


Figure 3. One of several approaches for loading an eggcrate with QW films.

III. Measured Quantum Well Thermoelectric Power Factor

In Fig. 4, we have plotted power factor, α^2/ρ values that have been obtained on N type Si/SiGe and P type B_4C/B_9C . These are based values measured at Hi-Z, NRL and PNNL [6]. As can be seen, the power factors (α^2/ρ) are about an order of magnitude higher than the best Bi_2Te_3 based alloys. Obviously, these materials are real challenges to replace bulk materials, as Hi-Z scales up the film deposition process and fabricates them into modules and devices.

The biggest problem with the measurements is separating the film properties from the composite (*i.e.* film + substrate) properties. For α and ρ this has been of little concern since the Si substrate has such a high electrical resistivity, its effect on the composite α and ρ is small. Therefore, to be conservative, we do not try to separate the film data from the substrate; we use the composite α and ρ data in all our design calculations.

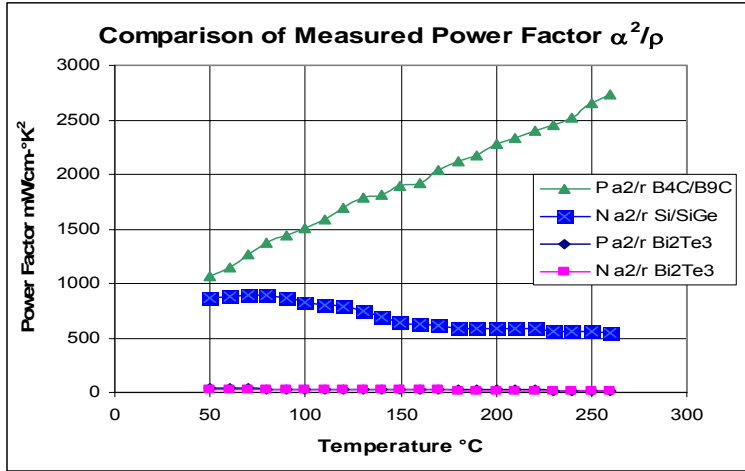


Figure 4. Measured Thermoelectric Power Factor of Quantum Well Materials is Significantly Higher than Current Bulk Bi_2Te_3 Thermoelectric Materials

IV. Performance Based on Published and Measured Quantum Well Thermal Conductivity

The thermal conductivity values, as with all thermoelectric materials, is the value that is hardest to pin down since the QW films are on a Si substrate. Therefore, we have concentrated on measuring thermal κ several different ways as shown in Table 1. We have measured both the N-type Si/SiGe and the P-type $\text{B}_4\text{C}/\text{B}_9\text{C}$ by the modified 3-omega technique and also deduced it from the efficiency data we obtained on the couple. As can be seen, we are obtaining close agreement with the two measured composite values. Theoretical papers have indicated the κ values of QW films should be $\sim 1/3$ of the bulk value and this is the value we list in the third column. These latter values are much lower (a factor of 2-3) than what we have measured on the composite samples because it does not include the Si substrate.

To be conservative, we have used published data on the bulk thermal conductivity of quantum well materials for predictions. As can be seen from Fig. 5, Kapton offers the lowest thermal conductivity substrate thus reducing parasitic heat losses.

Table 1. Room Temperature Thermal Conductivity Comparison for 11 μm Film on 5 μm Si Substrate

Composition	κ_c = Composite Thermal κ From Efficiency Measurement	$\kappa_{3\text{-omega}}$ = Composite Thermal κ From 3-Omega Method	$\kappa_{1/3}$ = Thermal κ From 1/3 of Published Bulk Value
Si/SiGe on Si Substrate	0.09 W/cm-K	0.10 W/cm-K	0.03 W/cm-K no substrate
$\text{B}_4\text{C}/\text{B}_9\text{C}$ on Si Substrate	0.10 W/cm-K	0.09 W/cm-K	0.05 W/cm-K no substrate

Fig. 6 shows Figure of Merit, $Z = \alpha^2/\rho \cdot \kappa$ values at 25°C calculated from data shown on Figs. 4 and 5. These quantum well thermoelectric Figures of Merit are significantly higher (5X to >10X) than current thermoelectric materials.

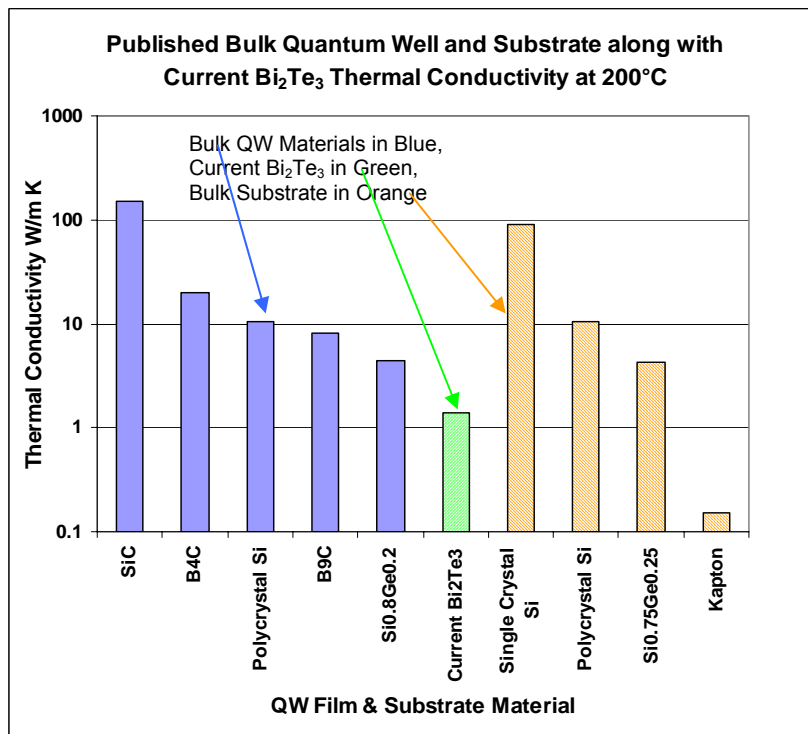


Figure 5. Comparison of Bulk Thermal Conductivity of Quantum Well Materials and Some Candidate Substrate Materials.

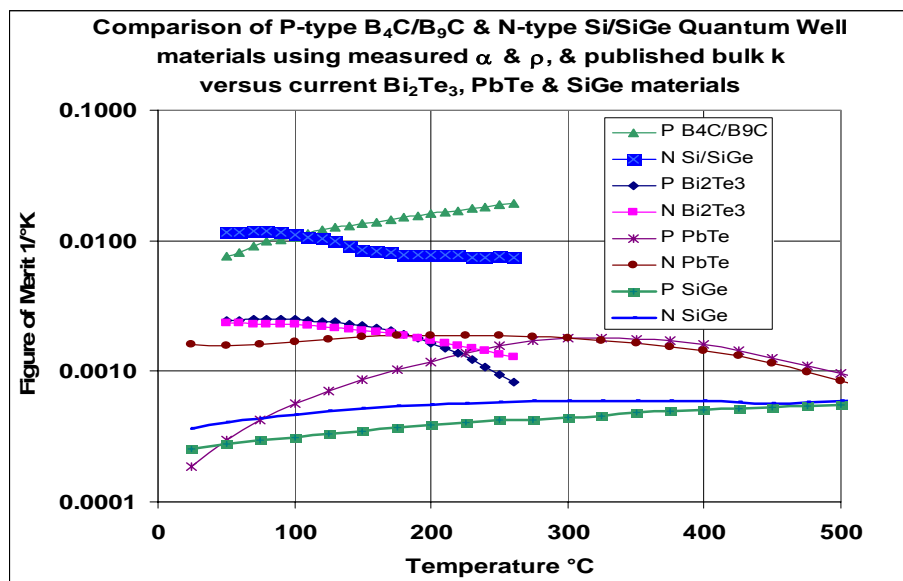


Figure 6. Figure of Merit of Quantum Well Thermoelectric Materials is 5 to 10X Higher than Current Thermoelectric Materials and Boron Carbides are Improving With Higher Temperature

V. Necessity to Reduce Quantum Well Film Substrate Thermal Losses

As noted, the substrate thermal conductivity has a substantial impact on the module efficiency. Based on Hi-Z's thermal models that include substrate, quantum well film, eggcrate and contact resistance, Hi-Z has predicted the efficiency of a module with a ΔT of 200°C as a function of substrate thermal conductivity. A 5 micron thick substrate is considered in Fig. 7 and a 25 micron substrate in Fig. 8. Both figures show that single crystal Si greatly reduces thermal to electric efficiency. However, a lower thermal conductivity 5 micron thick, SiGe substrate improves performance substantially but a much lower thermal conductivity 25 micron thick Kapton substrate improves performance even more. The thicker but lower thermal conductivity Kapton also provides a method to build a thermoelectric module with funneled heat [8]. The substrate and quantum well L/A provide an easy method to match the quantum well module thermal resistance with the thermal resistance of the waste heat.

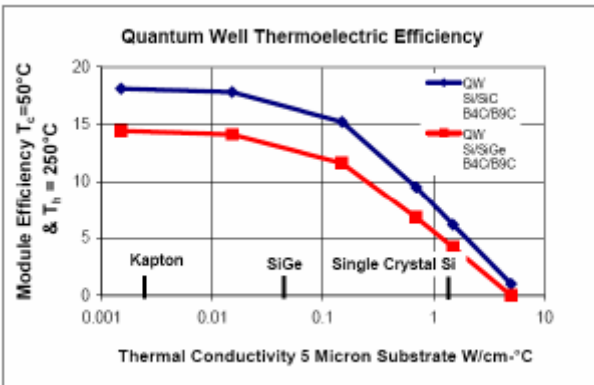


Figure 7. Quantum Well module efficiency as a function of a 5 micron thick substrate's thermal conductivity. Thermal conductivities close to SiGe or lower (0.05 W/cmK) provide substantial improvement. QW film is 11 micron thick.

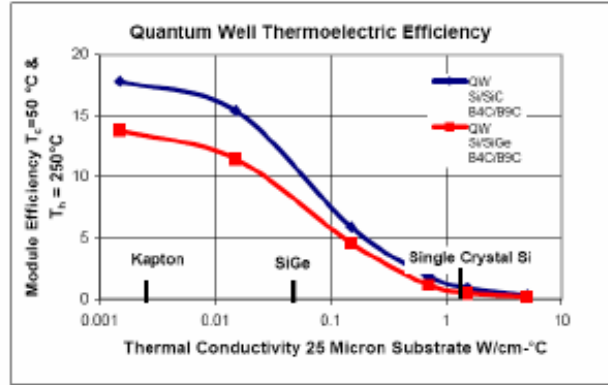


Figure 8. Quantum well module efficiency as a function of a 25 micron thick substrate's thermal conductivity. Thermal conductivities close to low κ Kapton (0.0015 W/cmK) provide improvement even on a 0.001 in. thick substrate. QW film is 11 micron thick.

IV. Energy Harvesting From Small Temperature Differences

Quantum well devices are suited for compact applications since a single N leg or P leg is only 11 microns thick on a 5 to 25 micron substrate, and the voltage for this couple is four times larger than a couple made with today's Bi_2Te_3 alloys. An example of a module design concept is shown in Fig. 9. This module will produce 10 mW of electrical power and an open circuit voltage of 6 V. The module is in the form of a flat disk. It will contain 25 semi-radial QW film legs with the N type Si/SiGe film deposited on one side of the substrate and P type Si/SiGe film on the other. These legs will be made by depositing the film through a mask. The legs will be made of multiple 100\AA thick layers. Electric connections can be made by either depositing metal on the inner and outer edges of the disk or by a plated through hole at each end of each leg. Some applications require a much larger number of legs, which are typically narrower than shown in Fig. 10, and for such case it may be preferable to use two or three sub-modules for the ease of manufacturing and making of electrical connections. The sub-modules will be stacked.

The main heat flow through this generator system is in the bottom and up the side, radially inward through the QW TEG module, up the center post to the heat sink above the module and into the pin fins where it is dissipated to the ambient air. A nylon screw is used between the bottom hot surface and the heat sink in order to minimize the bypass heat losses. A thin support tube, made of Vespel, or similar thermally insulating material, is used to separate the heat sink for the hot surface at the outer boundary in order to minimize the thermal bypass losses and to contain the internal thermal insulation

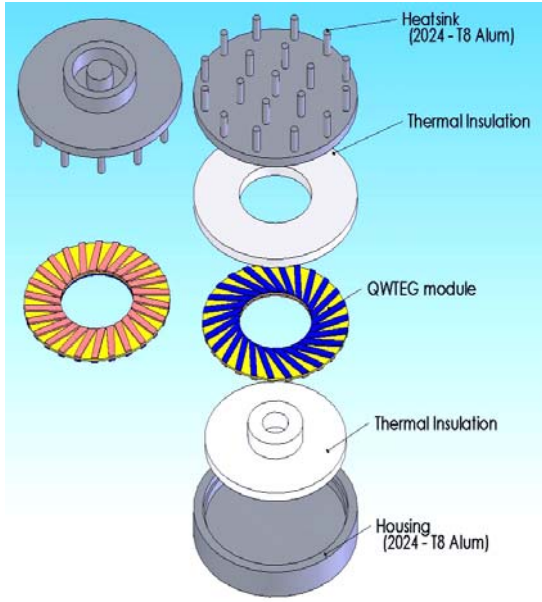


Figure 9. Components of the quantum well electric generator. Diameter is 1inch.

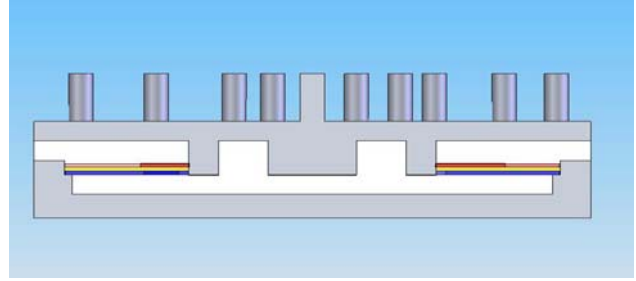


Figure 10. Components of the quantum well generator with radial heat flow.

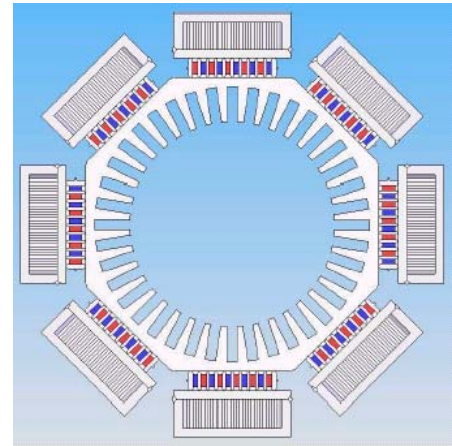


Figure 11. Cross section through hot waste heat source, quantum well modules and liquid heat exchangers. Outside diameter is 10 inches.

V. High Power Quantum Well Thermoelectric Generators

A typical arrangement of Hi-Z's quantum well thermoelectrics is in a cylindrical arrangement for a stack, engine exhaust, or producer gas application such as shown in Fig. 11. Since each quantum well module is flat, the modules could also be used as a refractory brick or heat exchanger section replacement. Thermoelectric power depends on the temperature difference across the thermoelectric module, and the "cold side" can be water, hot oil or air (forced or natural convection). With quantum well materials measured high temperature capability, water can be heated on the "cold side", near 100°C, to provide a source of hot water.

Predicted power and efficiency, based on quantum well measured material properties (Hi-Z, PNNL), for a typical single module are shown on Fig. 12 current voltage plot. This module is 2.35 in. x 2.35 in. square x 0.60 in. thick (same footprint as Hi-Z's HZ-14 commercial module) at the expected heat flux of 18 W/cm². For instance, to obtain one kW_e of power, 13 modules can be arranged in series. Another powerful method to improve power output

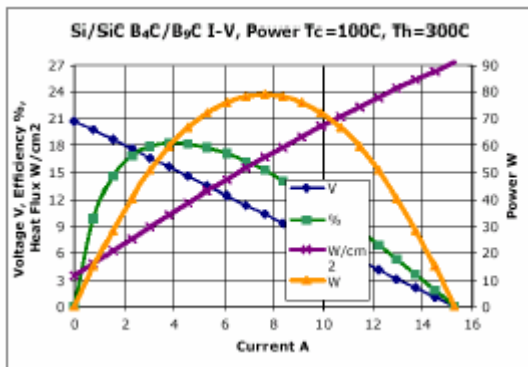


Figure 12. Predicted performance of a single 2.35 in. x 2.35 in. quantum well module where $T_H = 300^\circ\text{C}$, and $T_C = 100^\circ\text{C}$

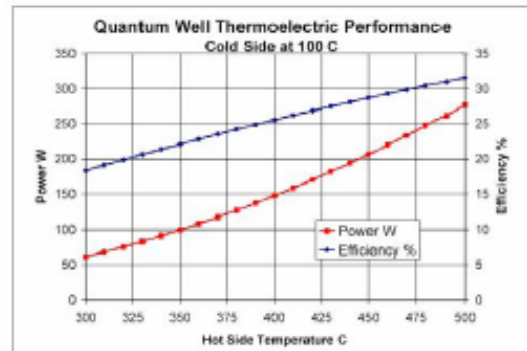


Figure 13. Predicted increase in maximum efficiency and power for a single 2.35 in. x 2.35 in. quantum well module

is to utilize the high temperature available in the waste heat stream. Many applications have temperatures $>700^{\circ}\text{C}$. Assuming a 200°C drop across a fluid film (measured in vehicle exhaust) the hot side of the thermoelectric could run at 500°C . A large increase in power is possible as shown in Fig. 13. Hi-Z needs to develop, design and fabricate a new high temperature module to realize these higher powers and efficiencies.

The thermoelectrics can easily be scaled in diameter and length to give more power. With quantum well materials, our predictions indicate that with hot gas at 500°C (300°C at thermoelectric hot side and 100°C at thermoelectric cold side) in a 5 inch flow path, a 5 kW_e generator can be packaged with 64 quantum well modules in a 30 in. long section with a 10 in. outside diameter. For use on a waste heat stream, the modules are loaded as shown in Fig. 14 between the finned hot side, and a liquid cold side heat exchanger. The 64 quantum well thermoelectric modules are individually loaded and coolant heat exchanges are arranged in a series (see Fig. 11) or parallel arrangement. The heated coolant can be used for heating, sanitation or hot oils for cooking.

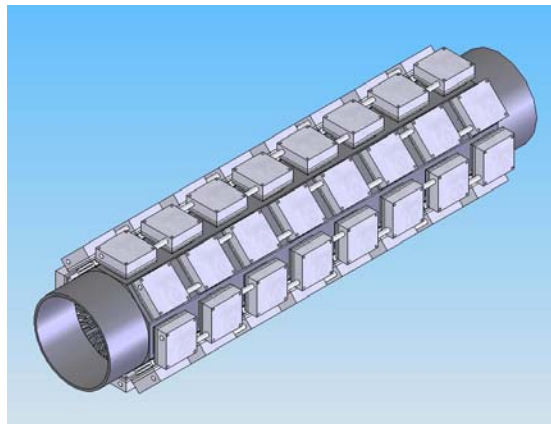


Figure 14. Arrangement of 64 quantum well modules with liquid heat exchangers on 5 in. ID stack.

VI. Summary

Figure 15 gives a summary of performance of Hi-Z's current commercial 14 Watt thermoelectric module and predicted performance of quantum well modules that give greater than 5X the voltage and power of Hi-Z's current commercial Bi_2Te_3 modules.

VII. Costs

Current bulk thermoelectric power modules are predicted to cost somewhat less than $\$1/\text{Watt}$ when produced in high volumes. Similar quantum well modules are predicted to cost less than $\$0.35/\text{Watt}$ in large volume production. A detailed cost analysis is underway. The cost of cooling modules will be somewhat less on a per watt basis. The reason for the predicted lower cost of quantum well devices is due both to their higher efficiency and the fact that they are made from lower cost raw materials than bulk thermoelectrics.

Hi-Z's current quantum well film production has been quite low because of the limitation of our laboratory equipment. Our current quantum well programs have allowed us to obtain a much larger sputtering machine. In addition, we are working with Pacific Northwest National Laboratory (PNNL) under the sponsorship of Department of Energy (DOE) to investigate production scale-up of quantum well films. Hi-Z is also investigating alternative means to fabricate quantum well films at higher rates.

Acknowledgments

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Thermoelectric Module Material	Temperature Difference °C	Voltage at Maximum Power	Maximum Efficiency %	Maximum Power W
N & P-type bulk Bi ₂ Te ₃	200	1.6	5.8	14
	Hi-Z's Commercial Alloys			
N type Si/SiGe & P-type B ₄ C/B ₉ C Quantum Well Kapton Substrate 25 μm thick	200	10.0	17	60
	250	12.4	20.9	72
	Under Development			
N type Si/SiC and P-type B ₄ C/B ₉ C Quantum Well SiGe Substrate ~5 μm thick (too hot for Kapton)	450	22.6	32.5	338
	Under Development			

Figure 15. Comparison of Quantum Well and Current Thermoelectric Performance