

## QUANTUM WELL THERMOELECTRIC DEVICES

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### ABSTRACT

Fabrication development of high efficiency quantum well (QW) thermoelectric continues with the P-type  $B_4C/B_9C$  and N-type Si/SiGe films. Si/SiC is being developed to replace Si/SiGe for higher temperature operation.

Both isothermal and gradient life testing are underway. One couple has achieved 700 hours at  $T_H$  of  $300^\circ C$  and  $T_C$  of  $50^\circ C$  with no degradation. Emphasis is now shifting towards couple and module design and fabrication. Preliminary design calculations regarding the development of actual quantum well modules will be presented for both power prediction and cooling applications. These modules can be used in future energy conversion system as well as air conditioning system designs.

### INTRODUCTION

Hi-Z Technology, Inc. (Hi-Z) is currently developing many different thermoelectric generator designs that are used to convert waste heat or heat sources directly to electricity. These include waste heat recovery from diesel trucks as well as automobiles and thermoelectric power generators including space application.

Bismuth telluride, PdTe, and SiGe based materials are presently used for power generation in remote locations, for example in deep space probes or direct conversion in general. However in most waste heat recovery and direct heat conversion applications an improvement in the efficiency of the energy conversion process from heat into electricity is needed. The efficiency of thermoelectric energy conversion devices is strongly limited by the performance of the materials, which is normally measured in terms of a *Figure of Merit Z* (see next section).

The breakthrough approach to increasing  $Z$  is to form compositionally modulated materials, mainly by QW confinement of carriers in the active layers in a multilayer film by adjacent barrier layers. The core concept is to enclose each electrically active layer by a material which has a band offset sufficient to form a barrier for the charge carriers. The major improvement in  $Z$  is expected to follow from an increased Seebeck coefficient that results from an increase in the density of states. There may also be a significant increase on the carrier mobility due to quantum confinement, so ideally there is an improvement in  $Z$  from the Seebeck coefficient, and the electrical conductivity. Also, the thermal conductivity, is reduced due to strain between

the QW and barrier layers which in turn inhibits phonon flow. QW effects become significant only when the thickness of the active layer is small, i.e., below about  $200D$ . The effectiveness of QW confinement and its effect on the figure of merit depends on many factors such as the carrier concentration, which is temperature dependent.

In addition to QW confinement, improvement in  $Z$  may result from the periodicity of the multiple film structure on the thermal conductivity [1]. At low values of the thickness of individual layers, there may be interference with the propagation of phonon modes, and therefore a reduction in  $\epsilon_L$ . The theory of this effect, and its application to both in-plane and cross-plane thermal conductivity values, is now a subject of intense research and may evolve into a field of engineered thermal transport independently of thermoelectricity [2&3].

### NOMENCLATURE

A	amperes	"	Seebeck coefficient
D	angstroms	$\delta$	thermal conductivity
k	kilo ( $10^3$ )	D	resistivity
m	milli ( $10^{-3}$ )	S	ohms
M	matching factor	:	micro ( $10^{-6}$ )
$T_C$	cold side temperature	W	watts
$T_H$	hot side temperature	V	volts
T	mean temperature	Z	figure of merit

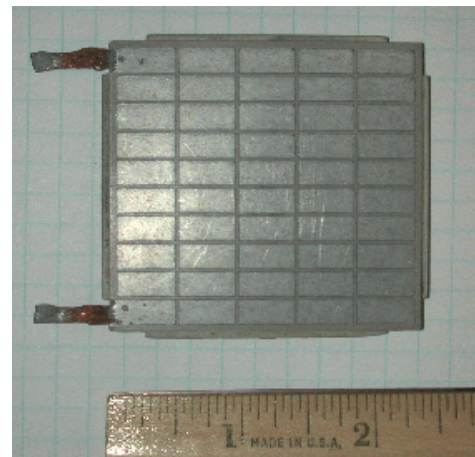


Figure 1. Hi-Z Thermoelectric Module

## RECENT ADVANCES

Hi-Z currently use conventional Bi<sub>2</sub>Te<sub>3</sub> alloy thermoelectric modules, as shown in Figure 1 [4]. The material in these modules has a value of ZT (figure of merit Z, times its mean absolute operation temperature T) of about 1. As shown in Figure 2, the value of ZT has hovered around 1 since the mid-1950s when semi-conductor materials were introduced into thermoelectric conversion. In the late 1990s new materials, including quantum well materials, were developed and value of 4 has been achieved with B<sub>4</sub>C/B<sub>9</sub>C and with some promise that even higher values can be obtained as development continues.

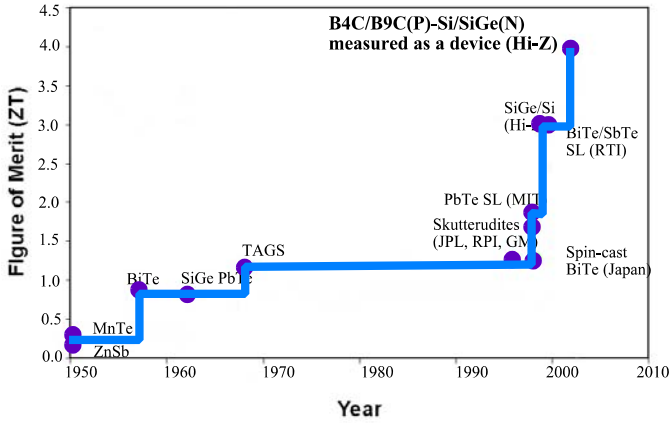


Figure 2. ZT Time Line.

The figure of merit (Z) for a thermoelectric material is obtained from its electric and thermal properties by

$$Z = \frac{\alpha^2}{D \cdot \epsilon} \quad (6)$$

where  $\alpha$  is the Seebeck coefficient of the material, V/K, D is its resistivity, ohm-cm, and  $\epsilon$  is its thermal conductivity, W/cm K. Efforts to improve the value of Z for a bulk material often fails because as one increases  $\alpha$ , the values of D and/or  $\epsilon$  usually also increase so that the resulting value of Z either remains the same or decreases. In 1992 Hicks and Dresselhaus [3] of MIT

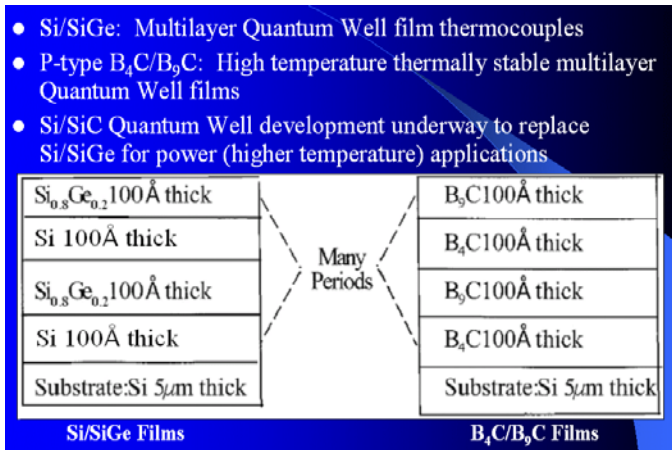


Figure 3. Construction of Quantum Well Films.

suggested that quantum wells should be a good candidate for thermoelectric energy conversion. This was confirmed in 1998

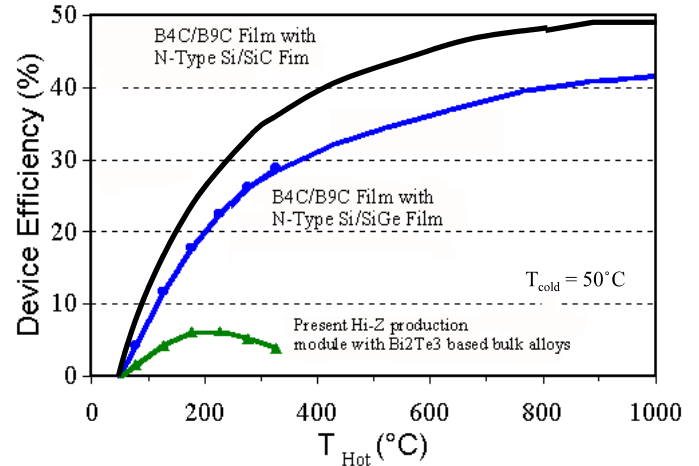


Figure 4. Calculated Couple Efficiency Versus Hot Side Temperature for B<sub>4</sub>C/B<sub>9</sub>C P-leg With a Si/SiGe N-Leg.

when Ghamaty and Elsner of Hi-Z [5] measured the thermoelectric properties of Si/SiGe quantum well films produced by both UCLA and the NRL for purposes other than thermoelectric energy conversion. Since then several investigators around the country have confirmed the improved thermoelectric properties of quantum well films [6].

Quantum well films have been made by several methods. The NRL and UCLA films measured by Hi-Z were made by molecular beam epitaxy (MBE). Currently Hi-Z is making its films by magnetron sputtering. Several other methods of film fabrication are possible. While magnetron sputtering does not result in quantum well films with thermoelectric properties quite as good as films made by MBE, they can be made much more quickly and therefore have the potential for much lower cost.

A quantum well film is formed by alternating thin (~100D) layers of two materials with differing electron band gaps such as Si and SiGe as shown in Figure 3. With these QW materials a large (factor of ~3) increase in  $\alpha$  and a reduction in  $\epsilon$  was observed in mid 1990s by Hi-Z and others [5]. These improvements resulted in a much improved Z and therefore an improved conversion efficiency ( $\eta$ ), which is defined by the equation:

$$\eta = \frac{T_H - T_C}{T_H} \times \frac{M - 1}{M + \frac{T_C}{T_H}}$$

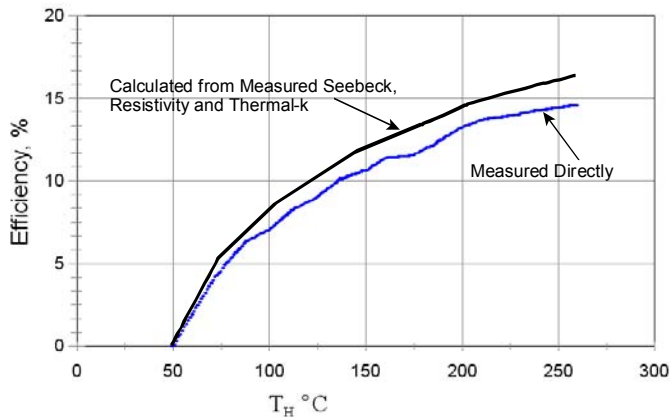
where the matching factor, M, is given by:

$$M = \sqrt{1 + \frac{Z}{2} (T_C + T_H)}$$

**Table 1.** QW Device Raw Test Data for 11  $\mu\text{m}$  Thick  $\text{B}_4\text{C}/\text{B}_9\text{C}$  and  $\text{Si}/\text{SiGe}$  on 5  $\mu\text{m}$  Si at  $T_C = 70^\circ\text{C}$  and  $T_H = 250^\circ\text{C}$ .

	Power Into Heater			Power Out From Couple			Efficiency
	Voltage	Current	Power	Voltage	Current	Power	
$\text{B}_4\text{C}/\text{B}_9\text{C}-\text{Si}/\text{SiGe}$	0.1413V	47.1 mA	6.657 mW	0.365 V	2.608 mA	0.952 mW	14.30%
Calibration: $\text{Bi}_2\text{Te}_3$ Alloys	2.510	0.836 A	2.098 W	0.034 V	3.15 A	0.107 W	5.10%

where  $T_C$  and  $T_H$  are respectively the cold and hot junction absolute temperatures. One will note that the first term of the efficiency equation is the Carnot efficiency.



**Figure 5.** Measured QW Couple Efficiency Versus Temperature.

The graph conversion efficiency as a function of  $ZT$  for various values of  $T_H$  and a value of  $T_C$  equal to  $50^\circ\text{C}$  [7], shows for even modest values of  $T_H$ , such as  $250^\circ\text{C}$ , and a value of  $ZT = 4$ , one can exceed a conversion efficiency of 20%.

A quantum well film useful in a thermoelectric module is made by making many periods of alternating 100D layers. These layers are typically formed on a substrate such as silicon, which can remain as part of the film. If the substrate does remain, it becomes a parasitic loss in the system. This problem is discussed later.

A quantum well couple was fabricated [7], that consists of  $\text{B}_4\text{C}/\text{B}_9\text{C}$  for the P leg and  $\text{Si}/\text{SiGe}$  for the N leg. Both legs are a total of 11  $\mu\text{m}$  thick QW films and were deposited on a 5  $\mu\text{m}$  thick Si substrate. The  $\text{B}_4\text{C}/\text{B}_9\text{C}$  QW films after deposition are annealed at  $1,000^\circ\text{C}$  where they interact with the Si substrate and the composite improves the thermoelectric properties significantly. The initial single crystal Si structure is no longer retained. Lower  $\delta$  substrates are being pursued to minimize the thermal losses. Figure 5 is a graph of the uncorrected module conversion efficiency as a function of the hot junction temperature and shows a conversion efficiency of over 14% at a  $T_H$  of  $250^\circ\text{C}$  and  $T_C$  of  $70^\circ\text{C}$ . No corrections were made for heat loss through the leads, by radiation, or through the substrate.

Table 1 presents the raw data taken both for the quantum well couple and a calibration couple made of bulk bismuth-telluride alloys taken on the same test rig.

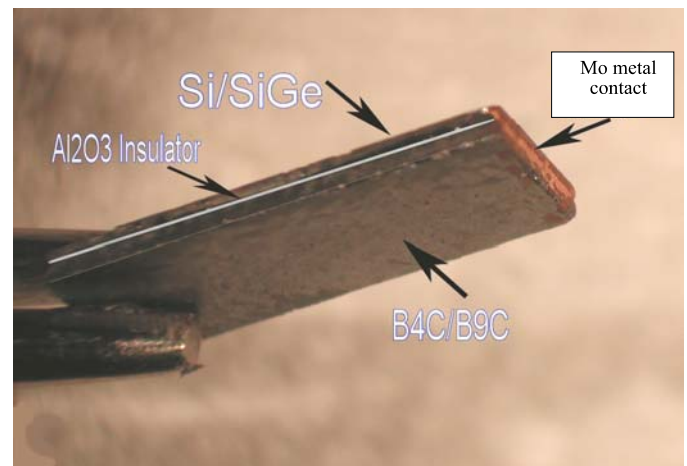
As previously mentioned, the substrate used will cause

parasitic losses. The calculated quantum well conversion efficiency as a function of film thickness for films deposited on a 5  $\mu\text{m}$  Si substrate is asymptotic to about 25% efficiency for an infinitely thick film [7]. Also, this calculation showed for ~20% conversion efficiency, the film thickness should be ~30  $\mu\text{m}$ .

Because the properties of  $\text{Si}/\text{SiGe}$  films fall off with increasing temperature, Hi-Z has also been depositing quantum well films of  $\text{Si}/\text{SiC}$ . This is a N-type quantum well material and can be used with the  $\text{B}_4\text{C}/\text{B}_9\text{C}$  P-type film for higher temperature applications. Thicker (~11: m)  $\text{Si}/\text{SiC}$  films will be fabricated on 5: m Si for the higher temperature  $\text{B}_4\text{C}/\text{B}_9\text{C}-\text{Si}/\text{SiC}$  device.

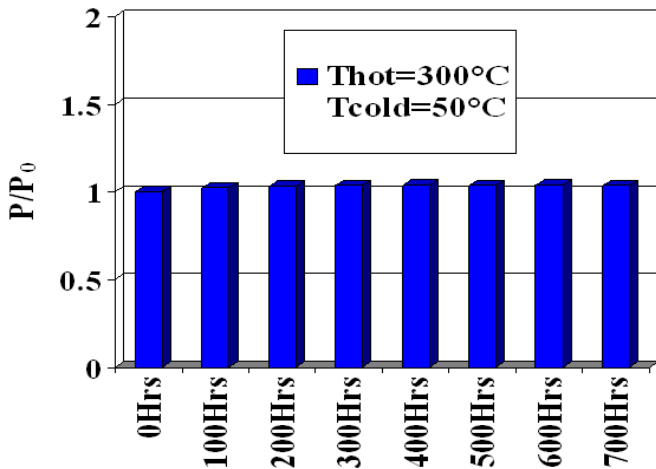
### MOLYBDENUM CONTACTED QW COUPLE

Figure 6 shows a recent QW couple with  $\text{B}_4\text{C}/\text{B}_9\text{C}$  and  $\text{Si}/\text{SiGe}$ . This couple was fabricated for a new round of thermal stability testing for high temperatures. An improved sputtering process was successfully developed to deposit the Mo metal contacts that exhibit a negligible contact resistance with both N and P material. The potential problem with contact resistance was previously highlighted but this newly developed sputtering process appears to demonstrate that this problem can be overcome and high efficiency modules can be fabricated.



**Figure 6.** QW  $\text{Si}/\text{SiGe}-\text{B}_4\text{C}/\text{B}_9\text{C}$  couple for thermal stability test (.2"X.8"). The Mo was deposited by an improved sputtering process. This is the first couple where an  $\text{Al}_2\text{O}_3$  insulator was used (.01" thick). Other oxides, such as stabilized  $\text{ZrO}_2$ , with much lower thermal conductivities will be incorporated in future couples.

Initial thermal stability testing of the Mo contacted couple at  $T_H=300^\circ\text{C}$  and  $T_C=50^\circ\text{C}$  for 700 hours showed very stable performance as shown by the very negligible change in power with time. Figure 7 shows these results which appear very promising. Also, isothermal testing of the individual  $B_4C/B_9C$  and Si/SiGe films up to  $600^\circ\text{C}$  for 800 hours has shown stable thermoelectric properties. We will continue the thermal aging for longer times and at several higher temperatures. More couples with metal contacts are being fabricated and will be life tested isothermally and in gradient operation to obtain power as a function of time.



**Figure 7.** Life testing of QW couple with Mo contacts. The power is obtained by measuring  $\alpha^2/D$ , where  $\alpha$  is the Seebeck coefficient, and  $D$  is the electrical resistivity. The slight increase in power is probably due to thermal annealing of the  $B_4C/B_9C$  which typically improves Seebeck coefficient in the first few hundred hours.

The room temperature resistance of this couple is very close (<5%) as compared to the calculated values of the N & P materials as shown in Table 2. The voltage output (at  $T\sim 5^\circ\text{C}$ ) of the couple near room temperature, also shown in Table 2, is also in agreement with the expected values.

**Table 2.** Thermoelectric properties of QW couple with Mo contact compared to calculated values. The Mo was deposited by a modified sputtering technique developed by Hi-Z.

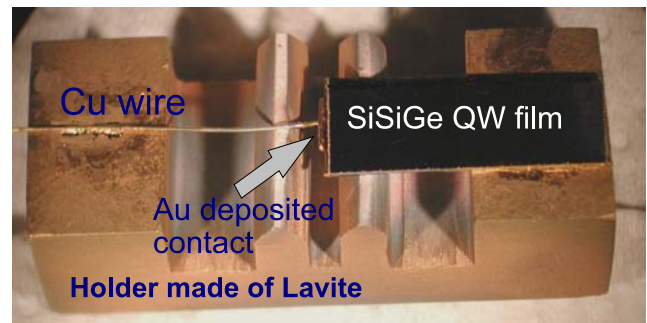
Room temperature properties	Measured	Calculated
Couple Resistance	1.23 kS	1.25 kS
Couple Voltage Output @ $T\sim 5^\circ\text{C}$	9.56 mV	9.60 mV

The significance of these couples with Mo contacts is that the Hi-Z developed by improved sputtering process was able to make good electric contact with all of the 1,100 QW layers in the 11  $\mu\text{m}$  thick film (each layer is 100D thick). It has been difficult to achieve this low contact resistance on some specimens in the past. Failure to contact each layer will typically lead to very high and/or

erroneous resistivities [8].

Based on prior Sandia studies with SiGe alloys, we expect Mo or W contacts to be stable at  $450^\circ\text{C}$  [8]. At a  $T_H$  of  $500^\circ\text{C}$  and  $T_C$  of  $50^\circ\text{C}$ , the calculated efficiency for a N-type Si/SiGe and P-type  $B_4C/B_9C$  module is  $\sim 18\%$ . When the Si/SiC QW are qualified with thicker films, we expect an efficiency of  $\sim 21\%$  at these same temperatures.

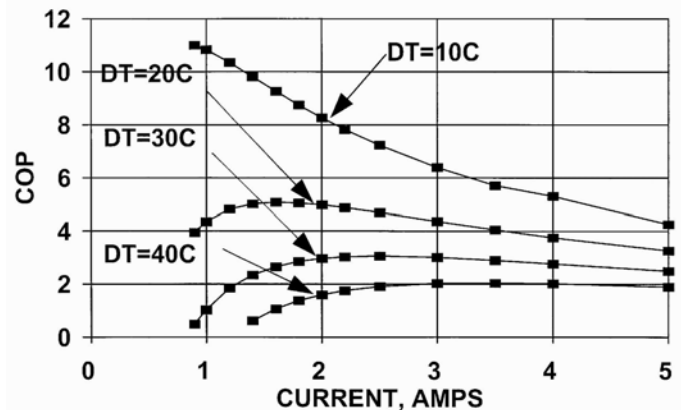
For higher temperatures (up to  $1000^\circ\text{C}$ ), Hi-Z plans to use the Si-Mo alloys as the contacting materials, which are the same materials used as the hot shoes in the SiGe multi hundred Watt generators. Hi-Z will also deposit these alloys by the improved sputtering process.



**Figure 8.** N-Type 11:  $\mu\text{m}$  thick Si/SiGe QW film on 5:  $\mu\text{m}$  Si substrate joined to a Cu wire operating as a cooler.

### Cooling

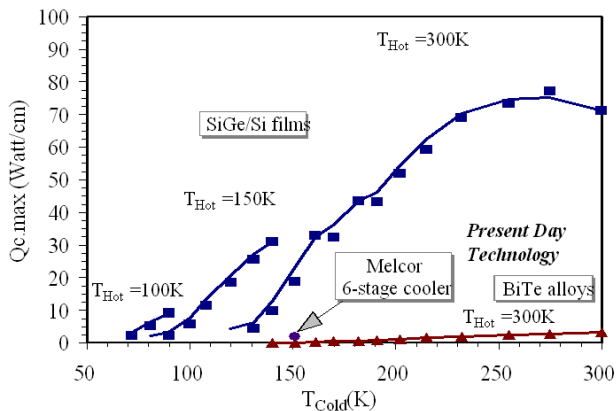
In a new experiment, the n-type Si/SiGe film was used as a cooler creating a maximum temperature difference of  $\sim 45^\circ\text{C}$ . This film was 11:  $\mu\text{m}$  thick on a 5:  $\mu\text{m}$  Si substrate. This temperature difference gives  $ZT\sim 3$  for  $T\sim 25^\circ\text{C}$ , for the QW film plus substrate combination. For this experiment, the N-type Si/SiGe was joined to a small Cu wire as shown in Figure 8. The QW film was the same material used in the couple mentioned above for the power generation.



**Figure 9.** COP of a 11:  $\mu\text{m}$  thick N&P Si/SiGe on 5:  $\mu\text{m}$  Si substrate Cooler as a Function of Current for Various Temperature Differences.

These properties of the Si/SiGe quantum well films indicate that they will make very good cooling modules. The maximum value of their figure of merit ( $Z$ ) peaks below room temperature

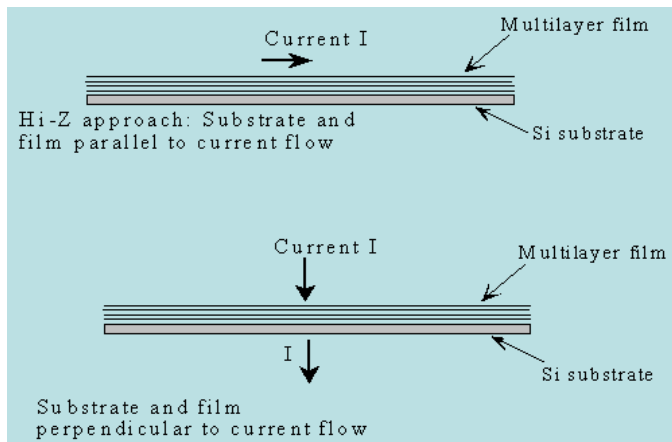
[2-4&9]. Design calculations for Si/SiGe cooling modules show a very high coefficient of performance (COP). Figure 9 presents a graph of the calculated COP for a Si/SiGe cooling module as a function of the module current, for temperature differences between 10°C and 40°C. The graph shows that the COP for this module should be 3.03 at a design current of 2.5A and at a temperature difference of 30°C. This compares to the COP as well as the maximum heat pumping rate, shown in Figure 10, of the best bulk Bi<sub>2</sub>Te<sub>3</sub> modules operating in this temperature range have a COP of about 0.5. The potential quantum well modules should be able to compete directly with mechanical refrigeration on a COP basis, but without either moving parts or CFCs. Such devices could be useful in the automotive industry to provide air conditioning.



**Figure 10.** Theoretical  $Q_c$  max (maximum heat pumping rate) of Si/SiGe film versus cold side temperature compared to Bi<sub>2</sub>Te<sub>3</sub> alloys.

### QW MODULE DESIGN CONSIDERATIONS

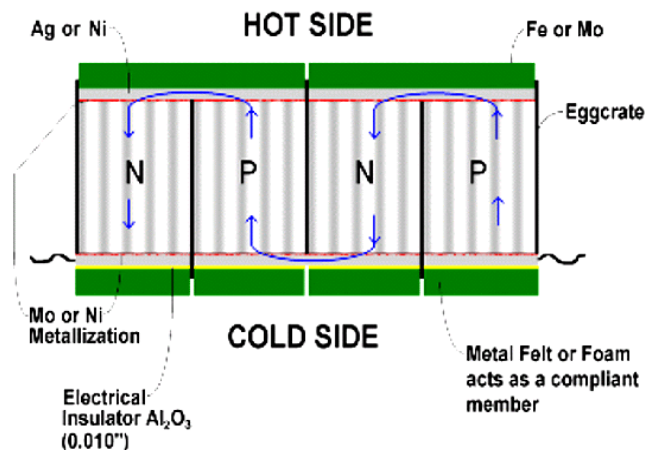
QW films can be used either in the direction of the deposited films or perpendicular to the direction of the films as discussed below and shown in Figure 11. In either direction an



**Figure 11.** QW films can be used parallel or perpendicular to current flow. However, higher Zs are obtained in the parallel direction. Due to QW behavior when used the perpendicular direction no QW enhancement is obtained but the  $\phi$  is lowered due to the many film interfaces.

improvement in Z usually occurs. However Hi-Z prefers the in plane use because (1) much higher Zs are achieved, because, all three thermoelectric properties  $\sigma$ , D and K are improved to yield a large increase in the figure 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 flux. However, the perpendicular direction requires a very high A/L, which imply very high and undesirable heat fluxes.

As shown in Figure 12 multiple pieces of the planar 11  $\mu$ m thick QWs can be assembled and loaded into an eggcrate. 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 [10] and proved satisfactory for accommodating thermal stresses.



**Figure 12.** One of several approaches for loading an eggcrate with QW films.

### COST

Current bulk thermoelectric power modules are predicted to cost somewhat less than \$1/Watt when produced in high volumes. Similar quantum well modules are predicted to cost less than \$0.20/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 size of our laboratory equipments. Our current quantum well programs have allowed us to obtain a much larger sputtering machine. In addition, we are working with Pacific Northwest National Laboratories (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, such as CVD, to fabricate quantum well films at higher rates.

## ACKNOWLEDGMENTS

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## REFERENCES

1. Harman, T.C., "PbTeSe/BiSb Short Period Superlattices as a New Thermoelectric Cooling Material," *Proc. 1st Natl. Thermogenic Cooler Conf., Center for Night Vision and Electro-Optics*, U.S. Army, Ft. Belvoir, VA, 1992
2. S. Ghamaty, N. Elsner, K. Wang and Q. Xiang, "Thermoelectric Performance of  $B_4C/B_9C$  Heterostructures", ICT 1996, Pasadena, California.
3. Hicks, L.D., Dresselhaus, M.S., "Effect of Quantum-Well Structures on the Thermoelectric figure of Merit," *Phys. Rev. B*, **47**, 19 (1993) 12 727-731.
4. "Proof-of-Principle Test for the thermoelectric Generator for Diesel Engines", 1991, Final Report, Hi-Z Technology, Inc., HZ 72691-1.
5. Elsner, N.B., Ghamaty, S., Norman, J.H., Farmer, J.C., Foreman, R.J., Summers, L.J., Olsen, M.L., Thompson, P.E. and Wang, K., 1994, "Thermoelectric Performance of  $Si_{0.8}Ge_{0.2}/Si$  Hetrostructures by MBE and Sputtering", Proceedings, 13<sup>th</sup> International Conference on Thermoelectrics, AIP Press, Kansas City, MO.
6. Martin, P.M. and Olsen, L.C., 2003, "Scale-up of  $Si/Si_{0.8}Ge_{0.2}$  and  $B_4C/B_9C$  Superlattices for Harvesting of Waste Heat in Diesel Engines", Proceedings, 9<sup>th</sup> DEER Conference, Newport, RI.
7. S. Ghamaty and N.B. Elsner, "Quantum Well Thermoelectric Devices", MRS, Boston, Mass., 2004.
8. Flinn, MRS Bulletin, Nov. 1995, pps. 70-73.
9. Ghamaty, S., 2002, "Quantum Well Thermoelectric Devices", Proceedings, DARPA/ONR/DOE High Efficiency Thermoelectric Workshop, Coronado, CA.
10. N.B. Elsner, "Review of PbTe Fabrication Techniques, MRS Vol. 234.