QUANTUM WELL THERMOELECTRICS FOR CONVERTING WASTE HEAT TO ELECTRICITY

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ABSTRACT

New thermoelectric materials using Quantum Well (QW) technology are expected to increase the energy conversion efficiency to more than 25% from the present 5%, which will allow for the low cost conversion of waste heat into electricity.

Hi-Z Technology, Inc. has been developing QW technology over the past six years. It will use Caterpillar, Inc., a leader in the manufacture of large scale industrial equipment, for verification and life testing of the QW films and modules.

Other members of the team are Pacific Northwest National Laboratory, who will sputter large area QW films. The Scope of Work is to develop QW materials from their present proof-of-principle technology status to a pre-production level over a proposed three year period. This work will entail fabricating the QW films through a sputtering process of 50 µm thick multi layered films and depositing them on 12 inch diameter, 5 µm thick Si substrates.

The goal in this project is to produce the technology for fabricating a basic 10-20 watt module that can be used to build up any size generator such as: a 5-10 kW Auxiliary Power Unit (APU), a multi kW Waste Heat Recovery Generator (WHRG) for a class 8 truck or as small as a 10-20 watt unit that would fit on a daily used wood fired stove and allow some of the estimated 2-3 billion people on earth, who have no electricity, to recharge batteries (such as a cell phone) or directly power radios, TVs, computers and other low powered devices.

In this quarter Hi-Z has continued fabrication of the QW films and also continued development of joining techniques for fabricating the N and P legs into a couple. The upper operating temperature limit for these films is unknown and will be determined via the isothermal aging studies that are in progress. We are reporting on these studies in this report. The properties of the QW films that are being evaluated are Seebeck, thermal conductivity and thermal-to-electricity conversion efficiency.

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2 INTRODUCTION

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.

Gradient life testing are underway. One couple has achieved 700 hours at T_H of 300°C and T_C of 50°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.

So far, all the life test data on Si/SiGe and B_4C/B_9C, show little or no degradation in temperatures from 25˚C up to 600˚C. However, cost studies done on another DOE/NTEL funded program in which United Technology Corporation (UTC) is the prime contractor and Hi-Z is subcontractor, show the cost of QW modules using thin Si substrate are prohibitively high ($\gtrsim$\$10/Watt even at high volume). Also, handling a thin Si substrate, like 5μm thick, is very difficult and suppliers are difficult to find. Therefore, Hi-Z is working with Pacific Northwest National Laboratory (PNNL) to fabricate the QW films on Kapton™ instead of the 5μm thick Si substrate. PNNL is also a team member in the UTC/DOE/NETL program. The new cost studies show QW modules using Kapton could cost $\lesssim$\$0.50/Watt, at high volume.

3 EXECUTIVE SUMMARY

In this quarter Hi-Z has continued fabrication of the QW films, performed design calculations on Quantum Well modules and thermoelectric properties and also continued development of joining techniques for fabricating the N and P legs into a couple. The upper operating temperature limit for these films is unknown and will be determined via the gradient aging studies that are in progress. We are reporting on these studies in this report. The properties of the QW films that are being evaluated are Seebeck, thermal conductivity and thermal-to-electricity conversion efficiency.

4 CORRELATION OF EXPERIMENTAL RESULTS

Substrate Thermal Conductivity

It is known that the single crystal Si substrate that is used with our N type Si/SiGe and P type B_4C/B_9C, is a partial thermal short but not to the degree it negates the 14% efficiency positive results we have reported. We have two recent peer reviewed papers in which our results have been accepted. The first paper is from the Fall 2003 Materials Research Society meeting in Boston and is published in the proceedings. The second paper, just recently approved, is to be presented in San Francisco in July at the ASME meeting on the use of nanostructured materials in energy conversion devices. Both papers are being forwarded separately.

Since the QW films must be deposited on some substrate, the challenge is to find a substrate that presents the lowest thermal conductivity and has other favorable properties such as Coefficient of Thermal Expansion (CTE). We know the P type B_4C/B_9C films react with the single crystal Si substrate during annealing at 1000˚C, which should cause a reduction in thermal κ in the Si. We are in the process of removing the Si/SiGe and B_4C/B_9C QW films from their substrates by ion milling and will then measure the thermal κ of these 5 µm thick Si substrates.

In Table 1, we have listed α and ρ values that have been obtained on N type Si/SiGe and P type B_4C/B_9C and we have included the values measured at NRL. 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 chosen materials are real contenders to replace bulk materials as we can scale up the film deposition process and fabricate 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, we don't try to separate the film data from the substrate to be conservative; we use the composite α and ρ data in all our design calculations.

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 2. We have measured both the N type Si/SiGe and the P-type B_4C/B_9C by the modified 3-omega technique and also reduced 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 ~1/3 of the bulk values 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. The property measurements results indicate the following:

1. The α and ρ composites show a factor of 10 improvement in the power factor α^2/ρ as compared with Bi_2Te_3 alloys. Quantum well material dynamics were initially predicted by Millie Dresselhaus and Ted Harmon at the Ft. Belvoir, VA thermoelectric meeting. However, Hi-Z is first in identifying and patenting Si/SiGe, B_4C/B_9C and Si/SiC as QW materials.
2. The thermal κ of our N and P composite materials are fairly low but it appears we can go lower by replacing the single crystal Si with fine grain Si or SiGe. Other substrate materials

include Kapton whose thermal κ is a factor of 100 times lower than Si. Kapton has a higher CTE than Si/SiGe or B_4C/B_9C but by depositing the films on both sides of the Kapton film, we should obtain a balanced structure. Our experience with depositing 1 μm thick Si/SiGe films on Kapton has shown very good thermoelectric properties, but from an on-going Navy funded program we think the double sided deposition will be required with thicker films. In the Navy program, we are fabricating our first quantum well device with N & P type Si/SiGe since it will operate near room temperature. It will produce 10 mW at 5V matched load and power a wireless sensor using waste heat at a T of ~ 40˚C. Another paper we plan to present in San Francisco discusses this QW power supply for wireless sensors and will also be forwarded.

3. With the B_4C/B_9C films, we can deposit them on Kapton. However, Kapton can not survive the post deposition 1000˚C anneal. On a new DOE sponsored program, we plan to investigate very short term annealing of specimens using lasers, rf heating, etc. to obtain successful B_4C/B_9C films without damaging the Kapton.

Table 3 shows ZT values at 25 ˚C calculated from Tables 1 and 2. Using measured power factor data, and published bulk thermal conductivity data with published adjustment of 1/3 κ for films, the third ZT column shows the Z of the QW films at room temperature. This shows the potential of these QW thermoelectric films with a ZT that is 5 to 10X greater than conventional materials. The first and second ZT columns show the ZT values at room temperature when using the composite thermal conductivity of the substrate and film.

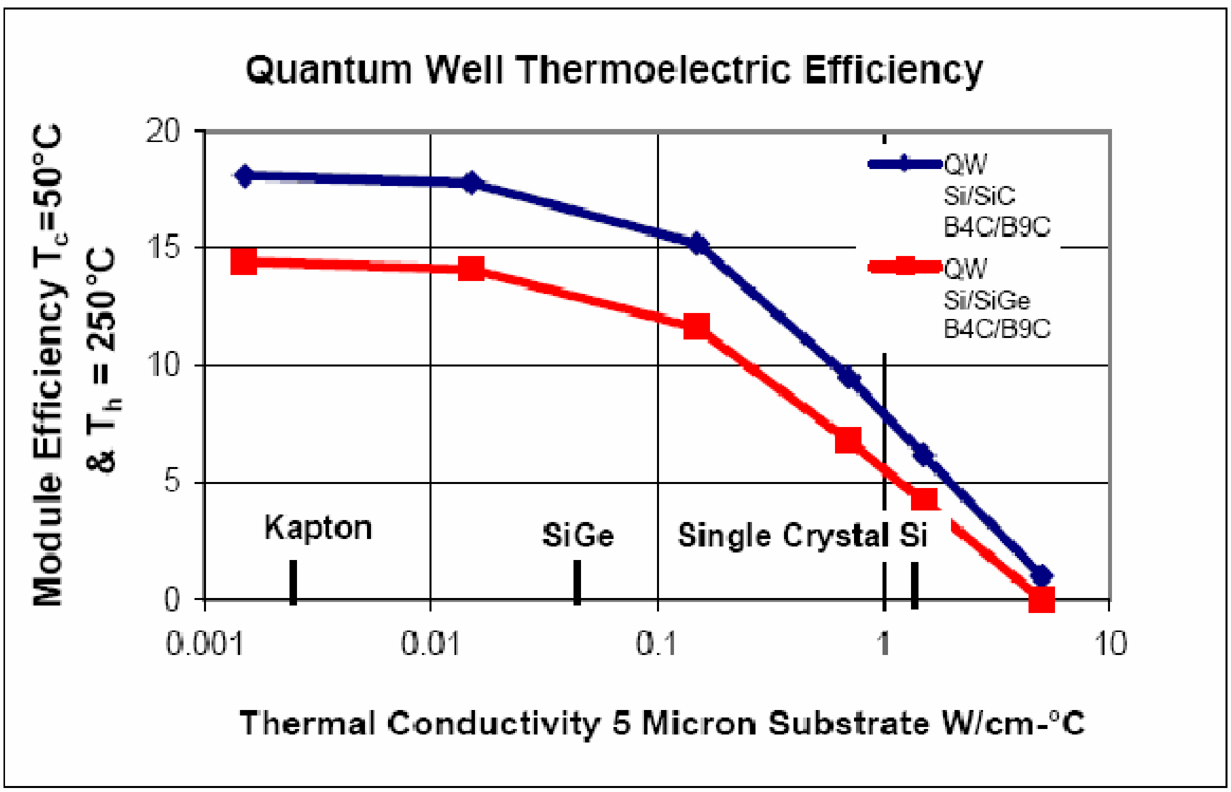

Figure 1. Quantum Well Module Efficiency as a Function of a 5 Micron Thick Substrate's Thermal Conductivity. Conductivities close to SiGe (0.05 W/cmK) provide substantial improvement. QW film is 11 micron thick.

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 temperature difference of 200˚C as a function of substrate thermal conductivity. A five (5) micron thick Si substrate is considered in Figure 1 and a twenty-five (25) micron substrate in Figure 2. Both figures show that single crystal Si greatly reduces thermal to electric efficiency. However, at a 5 micron thickness, a SiGe substrate improves performance substantially and at a 25 micron thickness, a Kapton substrate greatly improves performance.

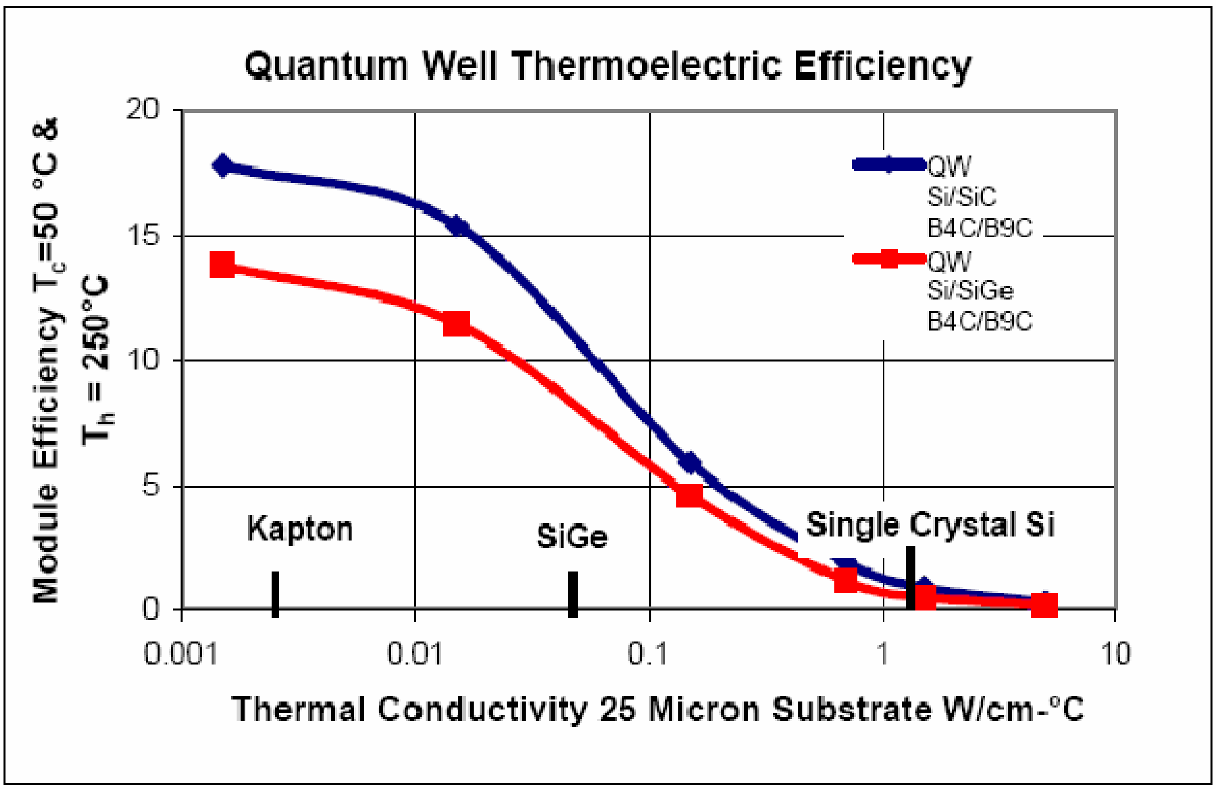

Figure 2. Quantum Well Module Efficiency as a Function of a 25 Micron Thick Substrate's Thermal Conductivity. Thermal conductivities close to low κ Kapton (0.0015 W/cmK) provide improvement even on a thick 1 mil substrate. QW film is 11 micron thick.

Table 1. TE Properties Comparison

The room temperature Resistivity (ρ) and Seebeck (α) were measured at the noted institutes.

Sample Composition	**Sample ID**	**Fabricated @**	**Measured @**	**α^2/ρ @ 25˚C (μW/cm-K^2)**
Si/SiGe	**HZ062**	**Hi-Z**	**Hi-Z**	**710**
	HZ062	**Hi-Z**	**NRL**	**605**
	2BK-S	**PNNL**	**PNNL**	**690**
	2BK-S	**PNNL**	**Hi-Z**	**686**
B_4C/B_9C	**HZ102**	**Hi-Z**	**Hi-Z**	**920**
	HZ102	**Hi-Z**	**NRL**	**891**
	1W-PB	**PNNL**	**Hi-Z**	**860**
	1W-PB	**PNNL**	**PNNL**	**822**
Bi_2Te_3 alloy	**-**	**-**	**Published**	**~80**

Table 2. 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
B_4C/B_9C on Si Substrate	0.10 W/cm-K	0.09 W/cm-K	0.05 W/cm-K no substrate

Table 3. ZT @ 25 ˚C of Si/SiGe and B_4C/B_9C. For comparison Bi_2Te_3 alloy has ZT of about 1 near room temperature

Composition	ZT using κ_c	ZT using $\kappa_{3\text{-Omega}}$	ZT using $\kappa_{1/3}$
Si/SiGe	2.2	2.0	6.7
B_4C/B_9C	2.6	2.9	5.4

Mo Contacts

We have fabricated a QW couple using N type Si/SiGe and P type B_4C/B_9C. It has operated for over 1,000 hours at a T_H of 300˚C and has exhibited stable performance as shown in Figure 3. With respect to QW materials for cooling applications, we expect to start a non-government funded 3 year effort qualifying the N and P type Si/SiGe materials for modules in air conditioning units. We have measured the α and ρ properties down to 4 K and the room temperature thermal κ as noted above. Based on these limited results, we feel Si/SiGe alloys might perform better (a higher COP) than existing mechanical equipment.

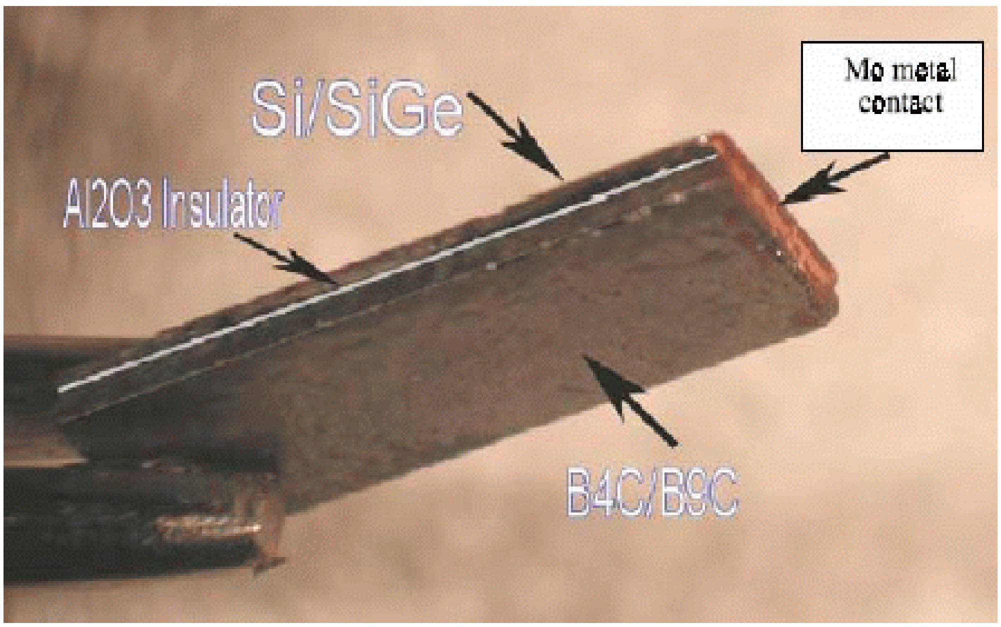

Figure 3. **QW Si/SiGe-B_4C/B_9C Couple for Thermal Stability Life Testing**. *The Mo was deposited by an improved sputtering process. With this first couple an Al_2O_3 insulator was used. Other materials, such as Kapton, with much lower thermal conductivities will be incorporated in future couples.*

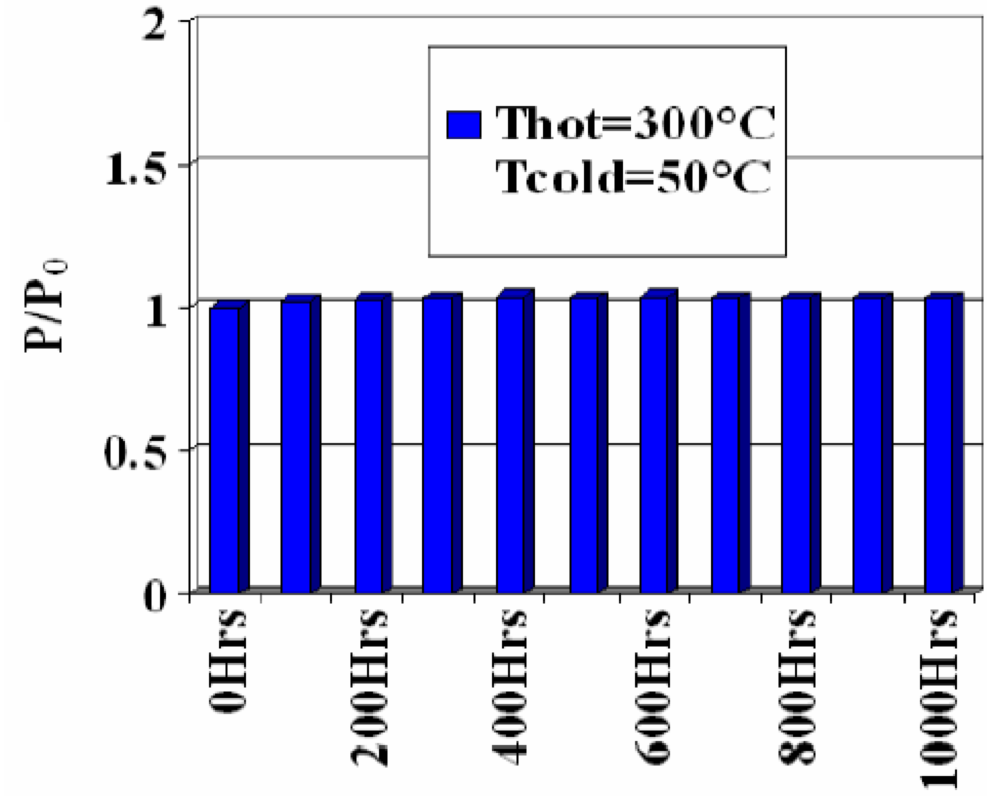

Figure 4. **Life Testing of QW Couple With Mo Contacts.** *The power is obtained by measuring* α^2/ρ *where* α *is the Seebeck coefficient, and* ρ *is the electrical resistivity.*

Table 4. As-fabricated Properties QW Couple.

Room Temperature Properties	Measured	Calculated
Couple Resistance	1.23 kΩ	1.25 kΩ
Couple Voltage Output @ T ~ 5 ˚C	4.56 mV	4.60 mV

The significance of these couples with Mo contacts is that the Hi-Z developed and improved sputtering process was able to make good electric contact with all of the 1,100 QW layers in the 11 μm thick film (each layer is 100Å 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 erroneous resistivities.

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 5. In either direction an 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 α, ρ 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.

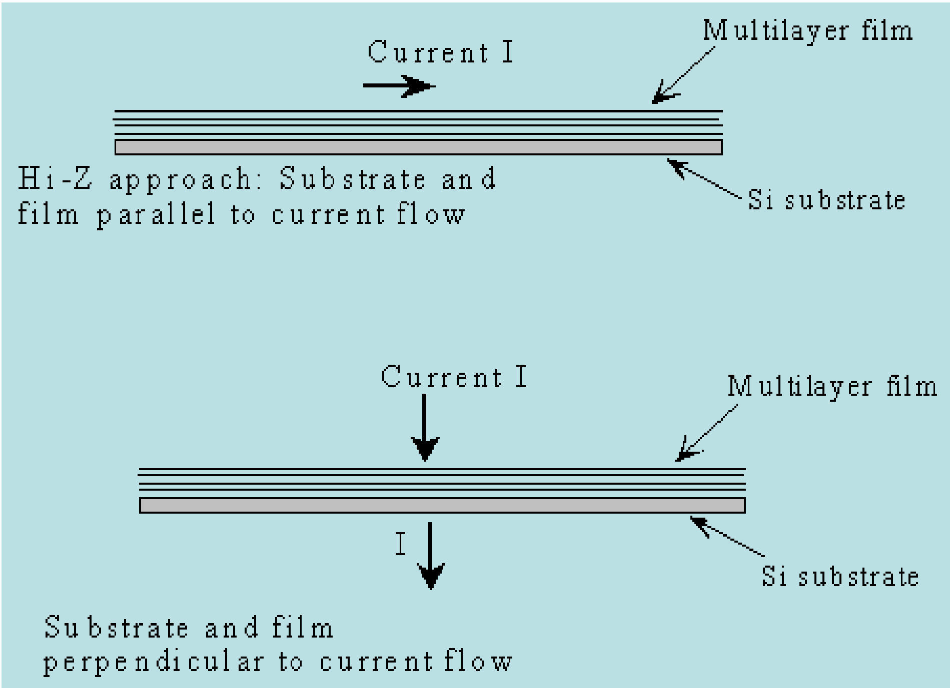

Figure 5. QW films can be used parallel or perpendicular to current flow. However, higher Zs are obtained in the parallel direction. Due to QW behavior when used the perpendicular direction no QW enhancement is obtained but the κ is lowered due to the many film interfaces.

As shown in Figure 6 multiple pieces of the planar 11 μm 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 alloys [10] and proved satisfactory for accommodating thermal stresses. Other approaches are and will be discussed in the next report. The cost studies are underway and indicating lower cost manufacturing are required.

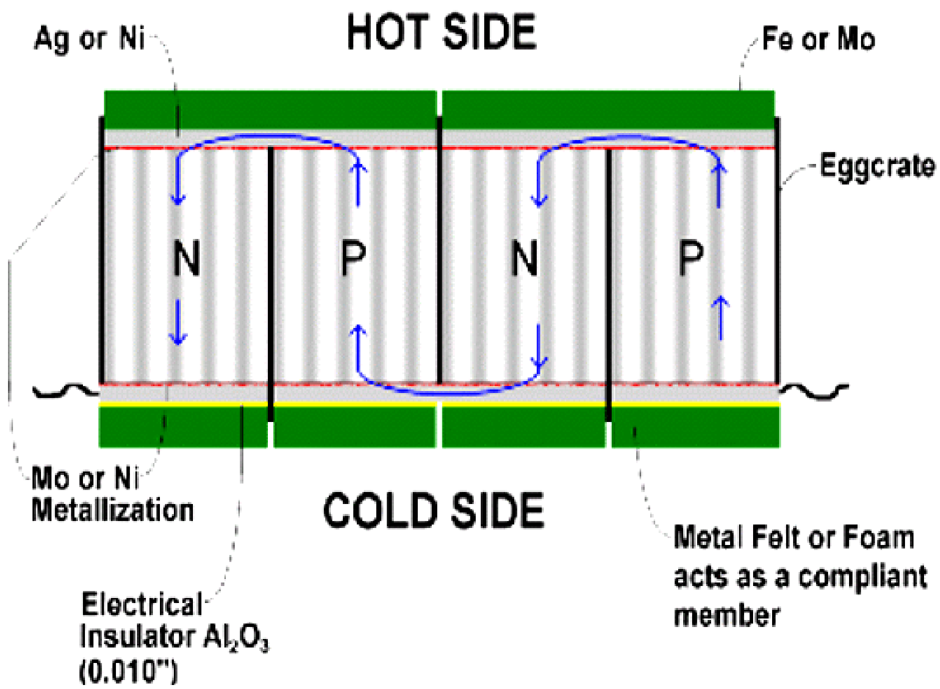

Figure 6. One of several approaches for loading an eggcrate with QW films.

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 $0.50/Watt in large volume production. A detailed cost analysis is underway on another NETL/DOE program in which UTC is the prime and Hi-Z is subcontractor. 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. Some of the results of this study (which this program predicated) are the following:

1. Si substrates, especially 5µm thick are very expensive.
2. Substrates such as Kapton are more appealing by improving efficiency and reducing costs.

Hi-Z's current quantum well film production has been quite low because of the size of our laboratory equipment. Our current quantum well programs have allowed us to obtain a much larger sputtering machine which arrived in February and will enhance production by June-July period. 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. The nanotechnology center at SUNY Albany, where NYSERDA funding has just begun deposition of Si/SiC films with Hi-Z as a subcontractor. They will be responsible for measuring the thermoelectric properties.

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