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QUANTUM WELL THERMOELECTRICS FOR CONVERTING WASTE HEAT TO ELECTRICITY

QUARTERLY TECHNICAL PROGRESS REPORT

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Submitted By

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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 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.

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1 LIST OF GRAPHICS

2 INTRODUCTION

Hi-Z is making progress on the development of a new type of thermoelectric conversion device called Quantum Wells (QW). Hi-Z has recently measured power and efficiency demonstrating a QW couple conversion efficiency of 14%, using a 11 μm QW film deposited on a 5 μm thick silicon substrate. The thickness of the films, area of deposition, and the method of joining N and P legs is the substance of this research and development effort.

3 EXECUTIVE SUMMARY

In this quarter Hi-Z started fabrication of thicker (>11 : m) QW films and also started 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. Fabrication of the films from the present 11μm with an efficiency 14% to the 30-50μm range with a possible efficiency of ~21%, is expected to be difficult since the added layers could induce stresses that will lead to warping or cracking of the films and the Si substrate. The sputtering techniques has been modified to develop these much thicker films. 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 PROGRESS BY TASKS/EXPERIMENTAL/RESULTS AND DISCUSSION/ CONCLUSIONS

Electrical Contacts for QWs
The requirement for contacts of the QW Si/SiGe-B_4C/B_9C are as follow:

- Low electrical resistance contact
- Use known compatible and conductive materials, e.g., metals Mo, W, Au, Ti.
- Control residual oxide at interface, e.g., interstitial sink; Si/SiGe, B4C/B9C, and Si/SiC all have tenacious oxide films that need to be penetrated.
- Thermal Stability- Avoid residual stress by expansion match, Avoid contact stress raisers, e.g., oxides, voids
- Provide ductility to absorb thermal stresses
- Strength - reduce source of stress; increase strength, e.g., SiC for solar cells Ni/WSi/Ti/Pt contacts. Auger spectroscopy shows oxygen peak in titanium as fabricated. This increases contact strength (and lowers electrical resistance)
- Life- Control growth of brittle, stress raising compounds, provide high strength to withstand thermal stresses

Sweet *et al* of Sandia evaluate W deposits for connections for SiGe thermoelectric materials. The effect of residual silicon oxide films and life determination were the principal areas of study. Useful insights were provided on several issues relative to QW requirements. The authors assumed a model where the retained oxide films at the W/Si20Ge interface were thin so that conduction by tunneling was an important contributor and where life was determined by growth of WSi_2. The SiO_2 was assessed to be 10-15D by Auger spectroscopy. The time to rapid increase in resistance under isothermal holds followed an Arrhenius relationship with the activation energy following that expected for W/SiGe formation from the elements.

The thin, uniform oxide film model was disproved by a doubling of resistance as film thickness went from 10 to 15D. A tunneling mechanism required a 35X increase. The improbability of the model was supported by the statement that the assemblage was made by "press bonding". This will lead to mechanical damage resulting on a classical electrical contact such as that described by Ragnar Holm (Electrical Contacts). Further, a film of this thickness is thermodynamically unstable because of the high surface-to-volume relationship; such instability leads to spheroidization to reduce surface energy as discussed by Flynn.

The classical electrical contact consists of disconnected, partially spheroidized particulate oxide with conductive elements in contact in the intervening areas.

The authors show a slow increase in resistivity followed by a much more rapid increase at a critical time that was independent of the thickness of the tungsten in the range 1-3 µm. Transition to the rapid increase time followed an Arrhenius relationship related to WSi_2 formation. This occurred at a critical thickness of WSi_2 equal to approximately 200D with local unbonding and complete loss of adhesion.

The authors show evidence of cracking once the contact resistance had risen to high values.

Review of the system indicates that tungsten (COE 4.3 x $10^{-6}C^{-1}$) is a close match to Si-20Ge (estimated 3.2 x $10^{-6}C^{-1}$) whereas molybdenum is not as close a match (5 x $10^{-6}C^{-1}$). On the other hand, WSi_2 was the only phase found by the authors (COE is 7.9 x 10^{-6} and the closely related $MoSi_2$ is 8.25 x $10^{-6}C^{-1}$). In contrast, molybdenum forms several intermediate silicides including the closely matched Mo_3Si (COE 4.3 x $10^{-6}C^{-1}$) so that disilicide formation will lead to high stresses in the W/Si-20Ge system.

It can be concluded that

1. Si-20Ge has a better expansion match for W- or Mo-based connector systems than Si.
2. The disilicide WSi_2 has a major mismatch in COE and will cause cracking and loss of contact.
3. It appears that a minimum thickness of WSi_2 is necessary to cause fractures in the W/Si-20Ge connector system. The lower expansion of Si (2.5 x $10^{-6}C^{-1}$) would be expected to result in fracture at a lower critical thickness of WSi_2.
4. The absence of intermediate (COE) silicides with tungsten observed by Sweet *et al* is a limiting factor in the life of these contacts.
5. Si-30Ge is probaly bether than Si-20Ge since more Ge will slow down WSi_2 formation

The authors do not discuss the mechanism of formation of WSi_2 if a continuous SiO_2 is present. In the more likely absence of such a continuous film, then WSi_2 will grow at all sites where W-to-Si(20Ge) contact occurs. Growth will be dependent on <u>rejection</u> of Ge (as no Ge is present in either silicide or oxide) so that diffusion away of the Ge may be a rate controlling step. This point, also, is not discussed by Sweet *et al.*

An interstitial sink (see Metcalfe and Dunning) for oxygen is frequently used in contacts (*e.g.*,Pt/Ti/WSi/Ni used for SiC-base solar cells). Removal of oxides from the interface will remove oxide stress concentrators that both weaken the connection, and increase the resistance. On the other hand, silicide formation can occur over the entire area. Nevertheless, there would seem to be a net advantage over a connection without an interstitial sink. We are preparing metal sprayed samples for contact with Mo which will be evaluated shortly.

Thermal Stability of Si/SiGe - B_4C/B_9C Couple

Figure 1 shows a new QW couple with B_4C/B_9C and Si/SiGe insulated with Alumina. Four couples were fabricated for a new thermal stability test for temperatures 300, 400, 500 and 600/C. A combination of sputter Au and Ag epoxy was used to make contact for the three couple and Mo metal was used for the fourth couple. Laser assisted sputtering was used to fabricate the Mo metal contact. As was mentioned on the previous reports, the joints are being made by silver epoxy and while this may be acceptable for low temperature service, long term low resistance stable bonds are needed for high temperature generation. Critical to this need is that each 100 D thick layer needs to be metallurgically contacted or “wetted” to obtain the lowest possible contact resistance.

Figures 2 through 7 show the latest isothermal data for the couples, the total aging time has been increased to 400 hours. The resistance ratio shown in the Figure 2 includes both the resistance of the both QW Si/SiGe plus B_4C/B_9C as well as the Ag conductive epoxy used to make the low resistance contact. As shown in these Figures 2-7 the data still supports that over 90% thermal aging effects are from contacts. Both Si/SiGe and B_4C/B_9C legs show very little change over the time even at 600/C (Figures 3, 4, 6 and 7). Developing low resistance electrical contacts to the QW materials of Si/SiGe to B_4C/B_9C at 400, 500, and 600°C are underway indicating little or no change in total electrical properties with time.

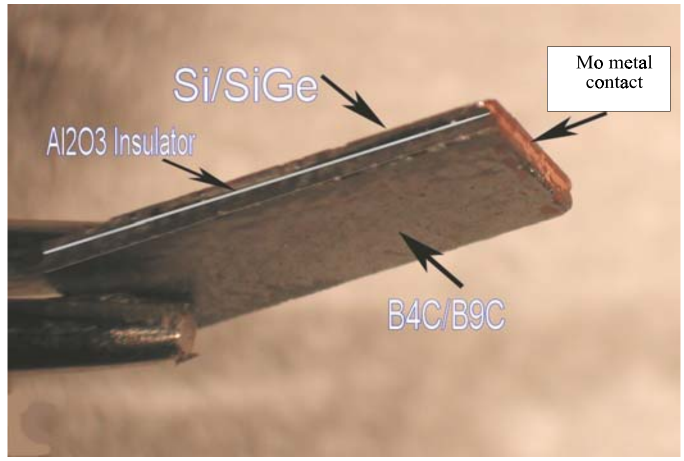

Figure 1. QW Si/SiGe-B_4C/B_9C couple for thermal stability test. The Mo was deposited by an improved sputtering process. This is the first couple where an Al_2O_3 insulator was used. Other oxides, such as stabilized ZrO_2, with much lower thermal conductivities will be incorporated in future couples.

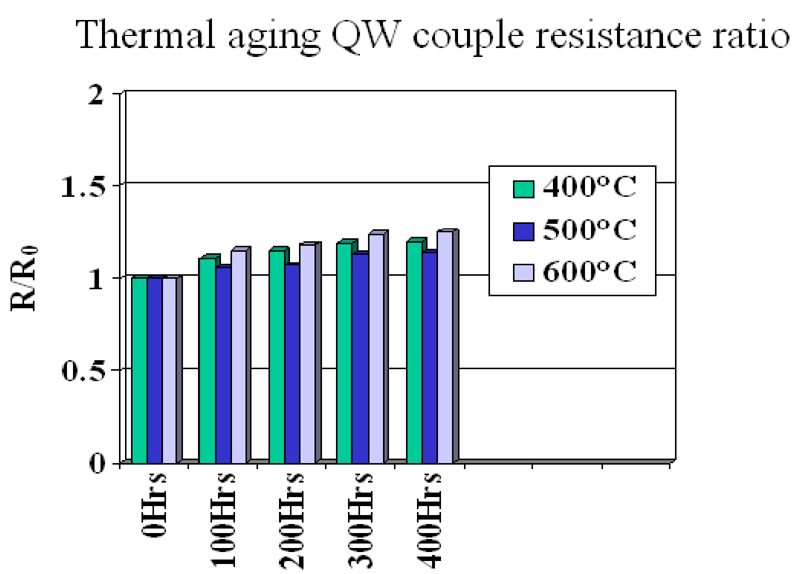

Figure 2. Isothermal aging studies of Si/SiGe - B_4C/B_9C couple.
Y-axis is the resistivity ratio at various aging time. The resistance ratio includes both the resistance of the QW Si/SiGe plus B_4C/B_9C samples as well as the Ag conductive epoxy used to make the low resistance contact. Individual aging of the contact and the QW films are shown in the following figures.

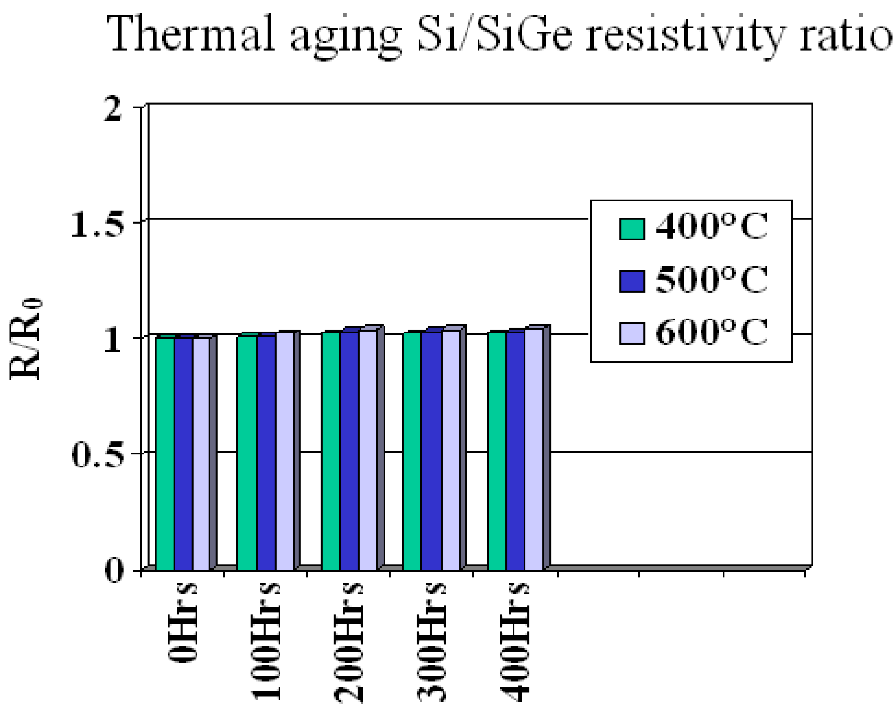

Figure 3. Thermal aging Si/SiGe leg.

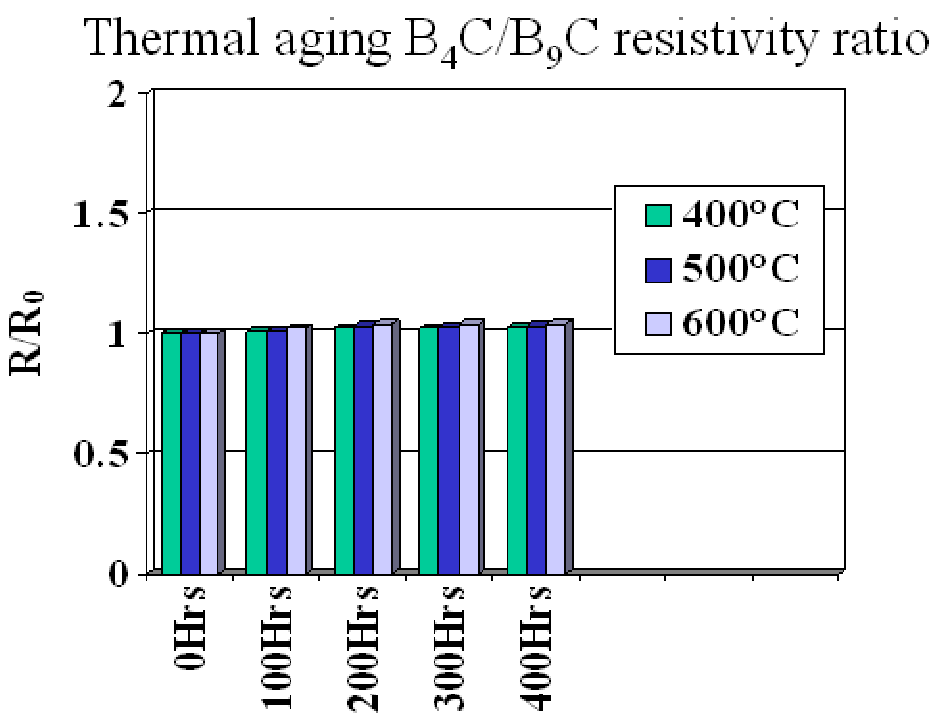

Figure 4. Thermal aging B_4C/B_9C leg.

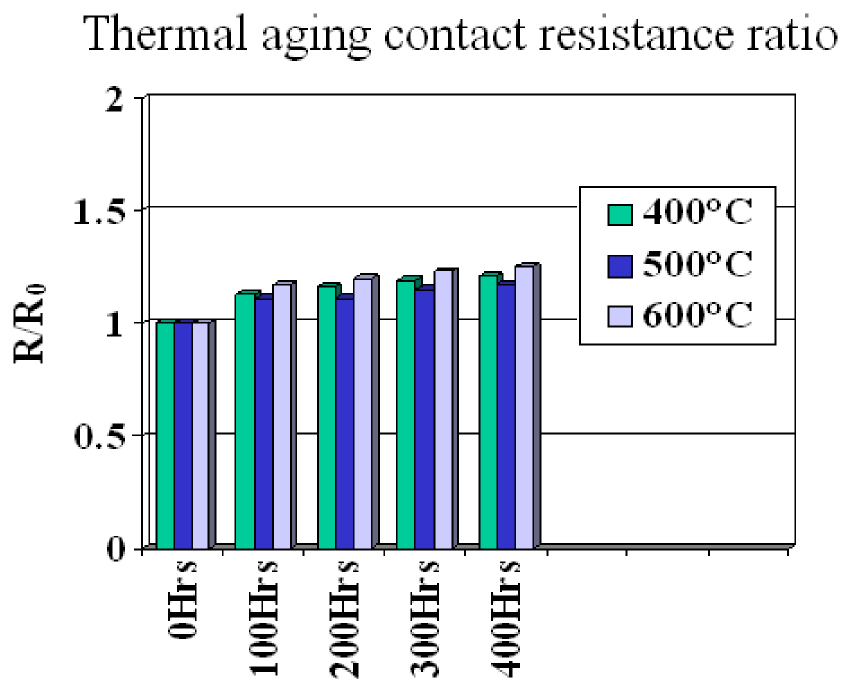

Figure 5. Thermal aging of sputtered Au and Ag epoxy.

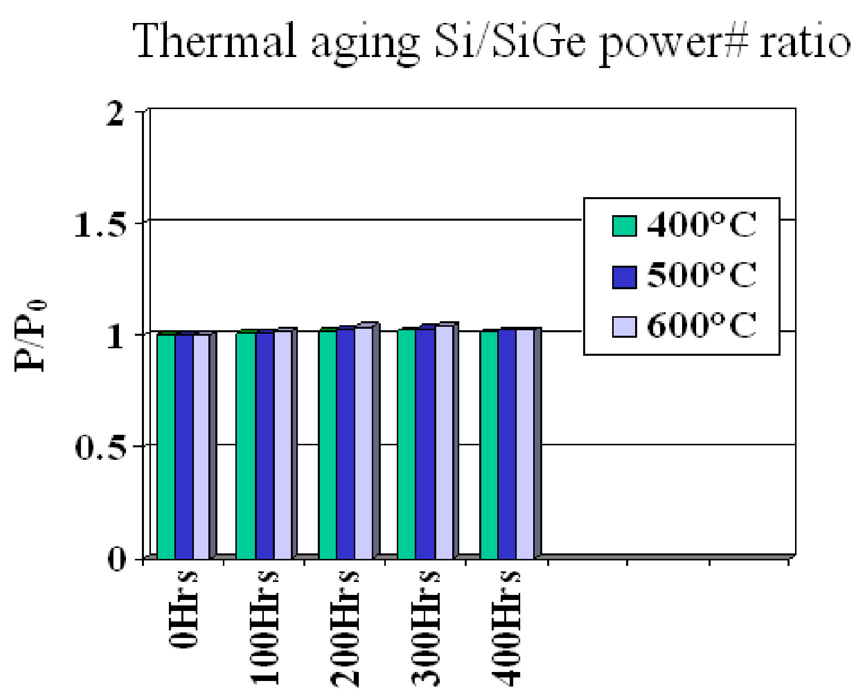

Figure 6. Thermal aging of Si/SiGe leg power number = " ^{2}/D

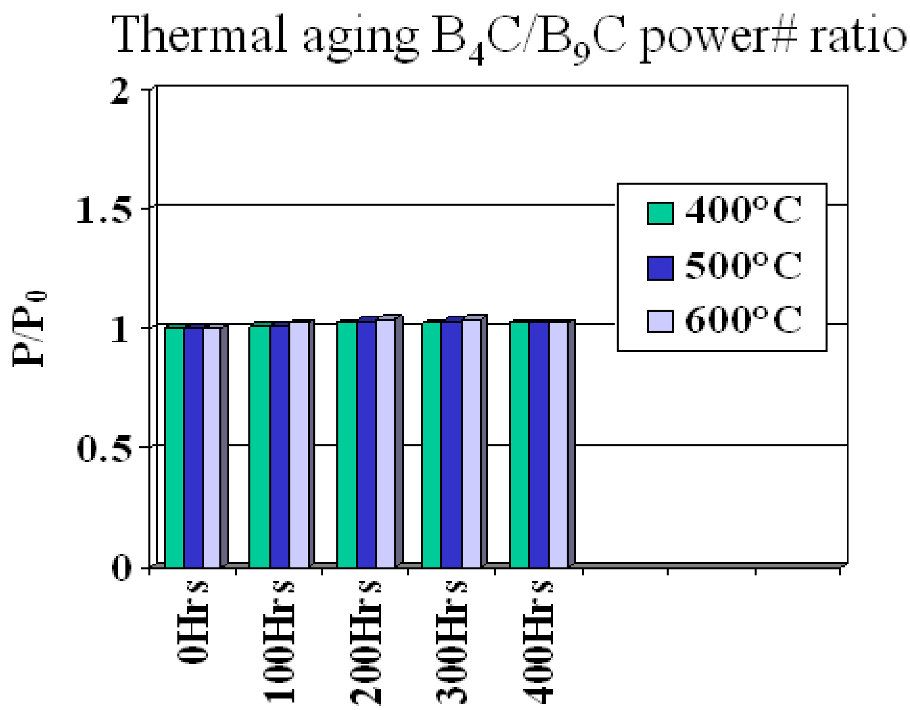

Figure 7. Thermal aging of B_4C/B_9C leg power number = "^{2}/D.

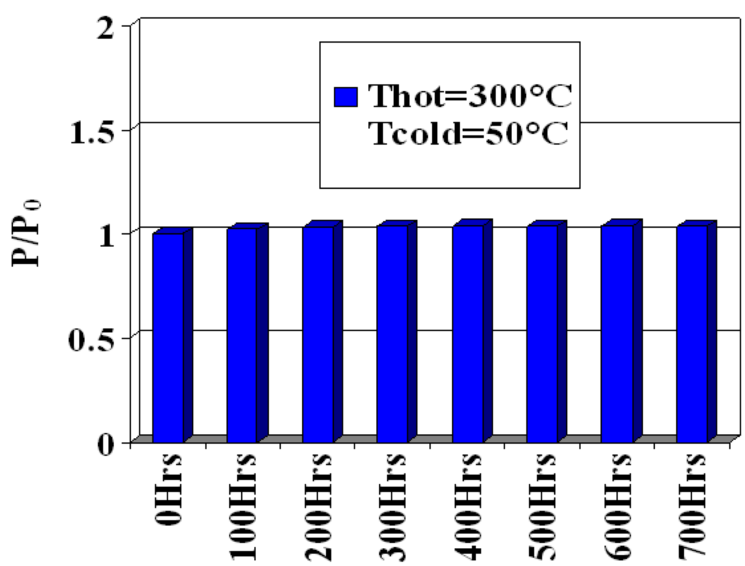

Figure 8. Life testing of QW couple with Mo contacts. The power is obtained by measuring "^{2}/D, where " is the Seebeck cofficient, and D is the electrical resistivity. The slight increase in power is probably due to thermal annealing of the B_4C/B_9C which typically improves in Seebeck coefficient in the first few hundred hours.

Mo Contacts

Figure 1 shows a recent QW couple with B_4C/B_9C and Si/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.

Initial thermal stability testing of the Mo contacted couple at T_H=300°C and T_C=50°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°C for 800 hours has shown stable thermoelectric properties, as shown in Figures 7, and 9-11. 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.

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 1. The voltage output (at) T~5/C) of the couple near room temperature, also shown in Table 1, is also in agreement with the expected values.

Table 1. Thermoelectric properties of QW couple with Mo contact compared to calculated values.

Room temperature properties	Measured	Calculated
Couple Resistance	1.23 kS	1.25 kS
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 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°C [8]. At a T_H of 500°C and T_C of 50°C, the calculated efficiency for a N-type Si/SiGe and P-type B_4C/B_9C module is ~18 %. When the Si/SiC QW are qualified with thicker films, we expect an efficiency of ~21% at these same temperatures.

For higher temperatures (up to 1000/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.

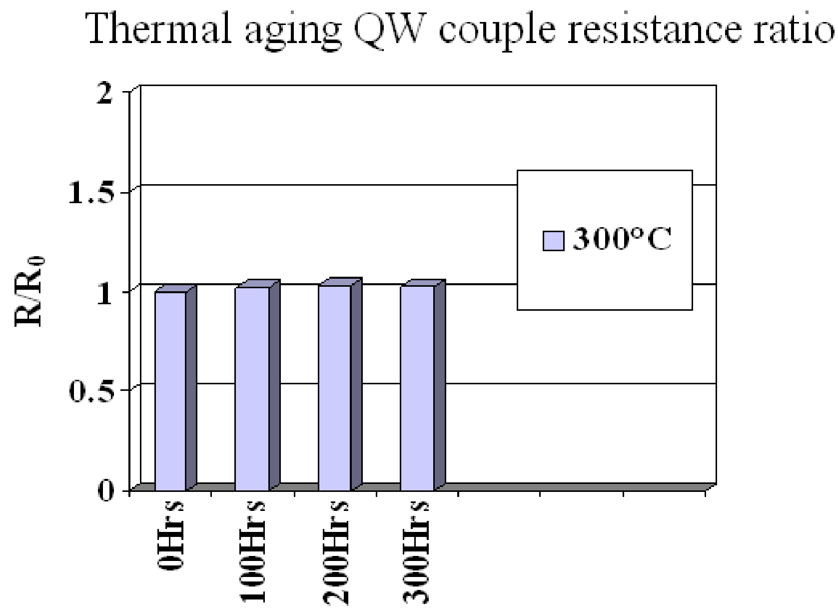

Figure 9. Isothermal aging studies of Si/SiGe - B_4C/B_9C couple.
Y-axis is the resistivity ratio at various aging time. The resistance ratio includes both the resistance of the QW Si/SiGe plus B_4C/B_9C samples as well as the Mo metal used to make the low resistance contact. Individual aging of the contact and the QW films are shown in the following figures.

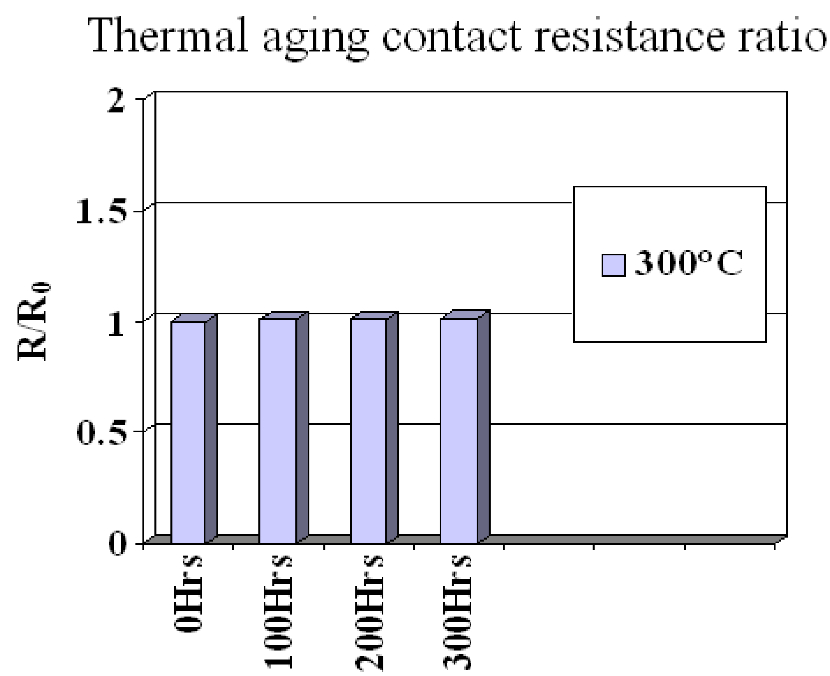

Figure 10. Thermal aging of sputtered Mo contact.

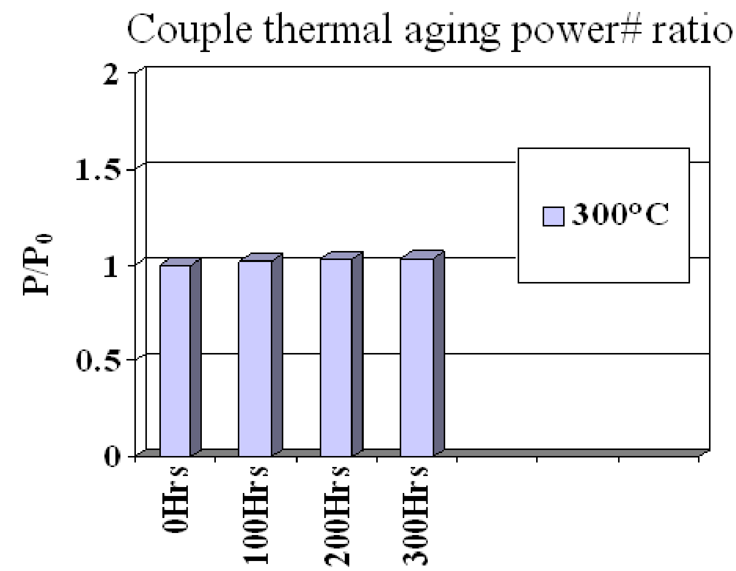

Figure 11. Thermal aging of QW couple with Mo contact power number = " ^{2}/D

Hi-Z Samples Comparison
Pacific Northwest National Laboratory (PNNL) with funding from the DOE has fabricated and measured and B_4C/B_9C and Si/SiGe samples. These samples were fabricated in the same way as the Hi-Z samples. The measured resistivity and Seebeck coefficient (done at PNNL) shows similar values as the Hi-Z samples. PNNL results are shown in Figure 12.

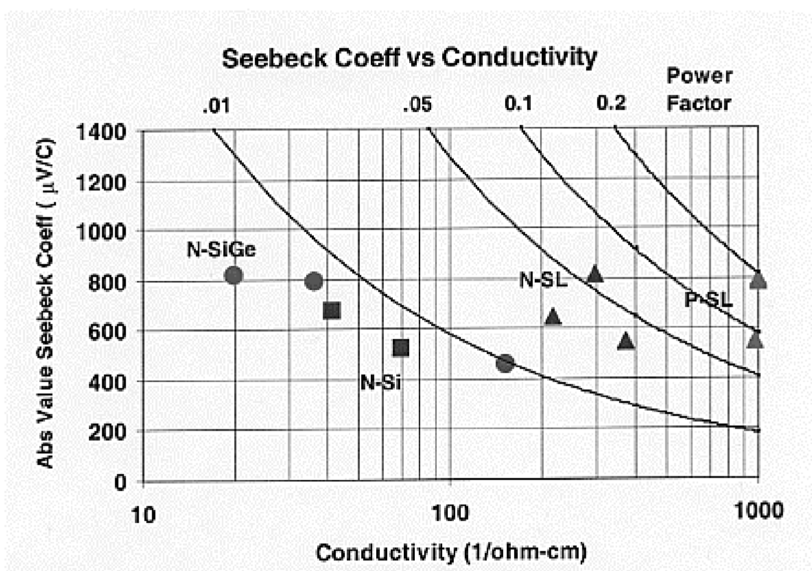

Figure 12. PNNL experimental results

Samples fabricated by Hi-Z were also measured by NRL, the results are shown in Figure 13. The results are also similar to the Hi-Z's and PNNL's results. Table 2 summarizes these comparisons.

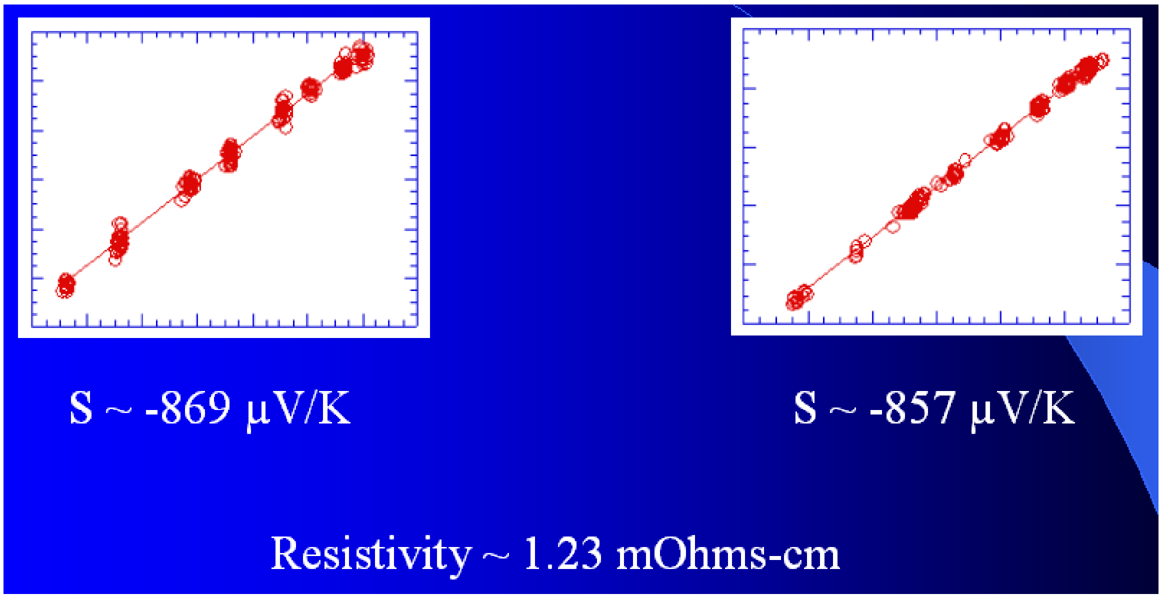

Figure 13. NRL Thermopower measurement of Hi-Z Si/SiGe Film on Silicon.

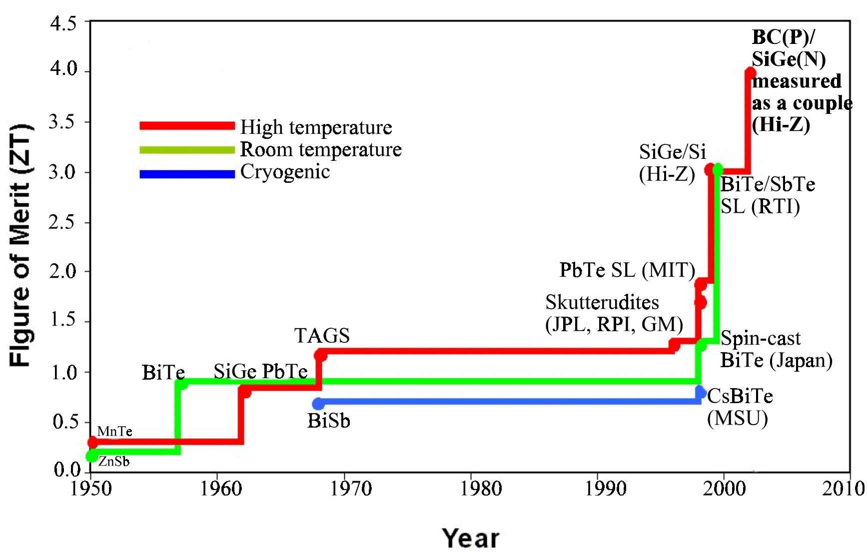

Figure 14. ZT Time Line

Table 2. TE Properties Comparison. The room temperature Resistivity (ρ)and Seebeck (α) were measured at the noted institutes but the thermal conductivity and high temperature α and ρ were only measured at Hi-Z.

Sample Composition	Sample ID	Fabricated @	Measured @	α^2/ρ @ 25/C (μW/cm-K^2)	ZT @ 25/C	ZT @ 150/C
Si/SiGe	HZ062	Hi-Z	Hi-Z	710	2.1	3.0
	HZ062	Hi-Z	NRL	605	1.8	-
	2BK-S	PNNL	PNNL	690	2.0	-
	2BK-S	PNNL	Hi-Z	686	2.0	2.6
B_4C/B_9C	HZ102	Hi-Z	Hi-Z	920	2.9	4.1
	HZ102	Hi-Z	NRL	891	2.8	-
	1W-PB	PNNL	Hi-Z	860	2.7	3.8
	1W-PB	PNNL	PNNL	822	2.6	-
Bi_2Te_3 alloy	-	-	Published	~80	~1	~1

As shown in Table 2, the Bi_2Te_3 alloys has a value of ZT of about 1. As shown in Figure 14, 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, started to increase the value of ZT to a out 4 (Table 2) with some promise that even higher values can be obtained as development continues.

The Sputtering Machine

The purchase of the 34" sputtering machine was completed The system was delivered and installed in February 2005. The system shown in Figure 15, was checked out by the PI. The final payment of $32,230 will be made upon operational checkout of the new sputtering machine in Hi-Z's facilities in March 2005. DOE ORO's payment of the agreed $100,000 share of the $322,300 total cost of the machine was received in the first week of January. NETL's agreed share of $105,000 was received January 16th. NASA's agreed share of $90,000 was received April 8, 2004 NAVSEA's share amounting to $27,300 will be billed to them in advance of the operational checkout and the final payment. The government funds awaiting the next disbursement to the fabricator are being held in a special interest-bearing money market account restricted to government funds.

Figure 15. Hi-Z new sputtering 34" diameter chamber processes up to (6) 8" wafers, (9) 6" wafers or hundreds of small substrates with up to 4 different materials. The system shown is fitted with 400/C backside quartz lamp heating, mag-lev turbo and a dry pump.

5 REFERENCES/BIBLIOGRAPHY/ACRONYMS

Any references and bibliography are as submitted in the proposal, pages 24 and 25. Acronyms and abbreviations are explained the first time they appear in the text.