

DOE AWARD DE-FC26-03NT41974

**QUANTUM WELL THERMOELECTRICS FOR CONVERTING WASTE HEAT TO
ELECTRICITY**

QUARTERLY TECHNICAL PROGRESS REPORT

REPORTING PERIOD 10-1-2005 THROUGH 1-31-2006

Submitted By

Hi-Z Technology, Inc.
7606 Miramar Road, Suite 7400
San Diego, CA 92126

Prepared By

Dr. Saeid Ghamaty, P.I
Email: Saeid@Technologist.Com
Phone (858) 695-6660
FAX (858) 695-8870

Issued February 2006

DISCLAIMER

“This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacture, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.”

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.

TABLE OF CONTENTS

- 1 List of Graphics
- 2 Introduction
- 3 Energy Harvesting Device
- 4 QW Couples Fabrication with Mo Contacts on Kapton and Si
- 5 References

1 LIST OF GRAPHICS AND TABLE

Figure 1. Components of QW generator.

Figure 2. Components of QW generator side view.

Figure 3. QW couples on Kapton.

Figure 4. QW couple on Si with Mo contact.

Figure 5. Life test data.

Table 1. Thermoelectric properties of QW device on Kapton with Mo contact compared to calculated values. Each N & P leg is 200 periods of Si/SiGe, and each layer is 100 Å thick. Each leg's area is ~0.07"× 0.2". The Kapton is 0.005" thick. The performance is compared to current bulk thermoelectric material

2 INTRODUCTION

Fabrication development of high efficiency quantum well (QW) thermoelectric continues with the P and N-type Si/SiGe films on Kapton and Si substrate.

Gradient life testing are underway. One couple has achieved about 3500 hours at T_H of 300°C and T_C of 50°C with no or little 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 (Ref. 1-8).

3 Energy Harvesting Device

As it was mentioned on the last report, 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 Figure 1. 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-

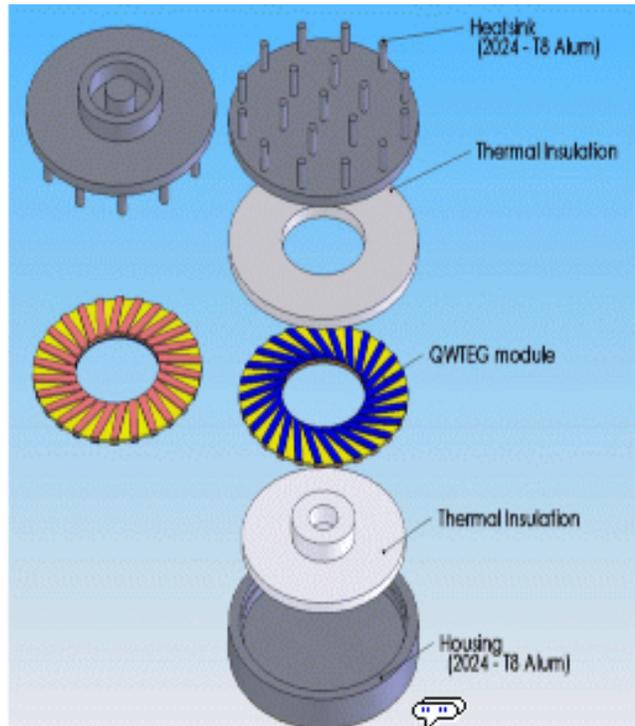


Figure 1. Components of the quantum well electric generator. Diameter is 2 inches.

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 100D 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 Figure 2, 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.

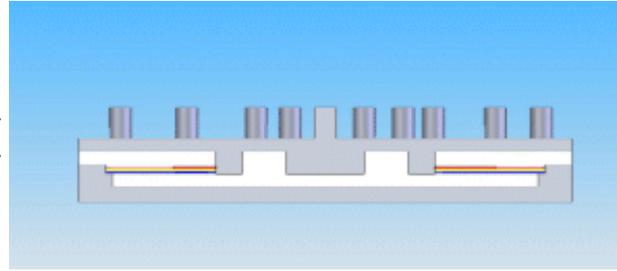


Figure 2. Components of the quantum well generator with radial heat flow.

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.

4 QW Couples Fabrication with Mo Contacts on Kapton and Si

Figure 3 shows a recent Quantum Well (QW) device with two couples of N and P-type Si/SiGe deposited on both sides of a Kapton™ substrate. This nanotechnology device is being fabricated for the U.S. Navy milliWatt energy harvesting applications. Only two out of twenty-six couples of the complete energy-harvesting device were contacted due to limited tooling and fixtures in the high vacuum chamber. An improved sputtering process was successfully developed to deposit the Mo

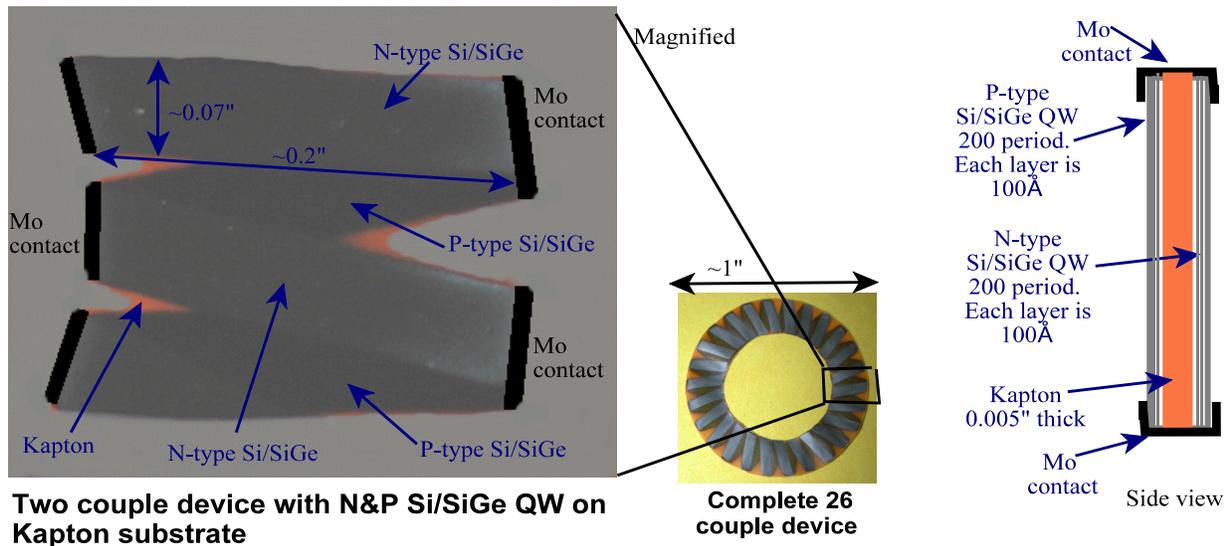


Figure 3. QW N and P-Type Si/SiGe two couple device on Kapton. The Mo was deposited by an improved sputtering process yielding the first QW device on Kapton. metal contacts that exhibit a negligible contact resistance with both the N and P material.

Table 1. Thermoelectric properties of QW device on Kapton with Mo contact compared to calculated values. Each N & P leg is 200 periods of Si/SiGe, and each layer is 100 Å thick. Each leg's area is ~0.07"× 0.2". The Kapton is 0.005" thick. The performance is compared to current bulk thermoelectric material

$T_{\text{Cold}} = 26^{\circ}\text{C}$ $T_{\text{Hot}} = 66^{\circ}\text{C}$	EXPERIMENTAL		CALCULATED	
	2 Couples Measured at) $T = 40^{\circ}\text{C}$	Results 2 Couples Measurements Extrapolated to 26 Couples at) $T = 40^{\circ}\text{C}$	26 Couples at) $T = 40^{\circ}\text{C}$	
			QW with $ZT \sim 3.0$	Bulk $(\text{Bi,Sb})_2(\text{Se,Te})_3$ with $ZT \sim 0.75$
Voltage (V_{oc})	225 milli V	2.93 V	3 V	0.5 V
Power	0.371 milli Watt	4.82 milli Watt	5 milli Watt	1.5 milli Watt

Initial measurements of power output from this Mo contacted device, from $T_{\text{cold}} = 26$ to $T_{\text{hot}} = 66^{\circ}\text{C}$, are shown in Table 1, and the results appear promising as they are close to the expected results. The output voltage from this device was 225 mVolt, and total power was 0.371 mWatt at a temperature difference of ~40°C. The power and output voltage of this device at the design) $T = 40^{\circ}\text{C}$, are very close (<10%) to the calculated values of the N & P materials. Extrapolating the two couple data to a full size device yields a total power of ~4.8mWatt @ ~2.93 Volt for a complete 26 couple energy harvesting device, enough power to operate a wireless sensor.

Assuming bulk thermal conductivity of the Si/SiGe films for evaluating this device, the ZT is calculated to be ~3 @25°C, which yields an efficiency of ~3% @) $T = 40^{\circ}\text{C}$. In comparison, a Bi_2Te_3 device would have a ZT of ~0.75 to 1.0 @25°C and a maximum efficiency of ~1.5% @) $T = 40^{\circ}\text{C}$ with no allowance for a substrate; with a substrate, the ZT and efficiency values would be even lower.

We plan to perform thermal aging of this device, and similar devices with metal contacts, such as Mo or other materials, and will be life testing samples both isothermally and in gradient operation to monitor power as a function of time at various operating temperatures. Also, extensive thermal cycling is planned to simulate anticipated usage. Alternate vacuum/coating equipment is being upgraded so we may complete the milliWatt device and fabricate multiWatt modules for the DOE and Army programs.

An earlier single couple device that was fabricated with N-type Si/SiGe and P-type B₄C/B₉C, is shown in Figure 4. It also has Mo contacts. However, the substrate with the N & P legs was single crystal Si and alumina was used to electrically insulate the N and P legs. It has operated for more than 3500 hours with no degradation (shown in Figure 5). The Si single crystal substrates have a high thermal conductivity and therefore are a major heat leak. Assuming bulk thermal- ϵ for the film the ZT of the couple without the Si substrate is calculated to be $\sim 4 @ 25^\circ\text{C}$. To reduce this heat loss and increase efficiency, Kapton is being pursued in place of Si since its thermal ϵ is \sim two orders of magnitude lower than Si. Kapton is also flexible, useful up to $\sim 300^\circ\text{C}$, and much lower in cost than 5: m thick Si. While Kapton has a higher coefficient of thermal expansion than Si/SiGe, deposition of the QWs on both sides of the Kapton helps balance out the differential thermal stresses. For temperatures above 300°C , Hi-Z is developing an inorganic materials approach that can operate at higher temperatures and minimize heat losses.

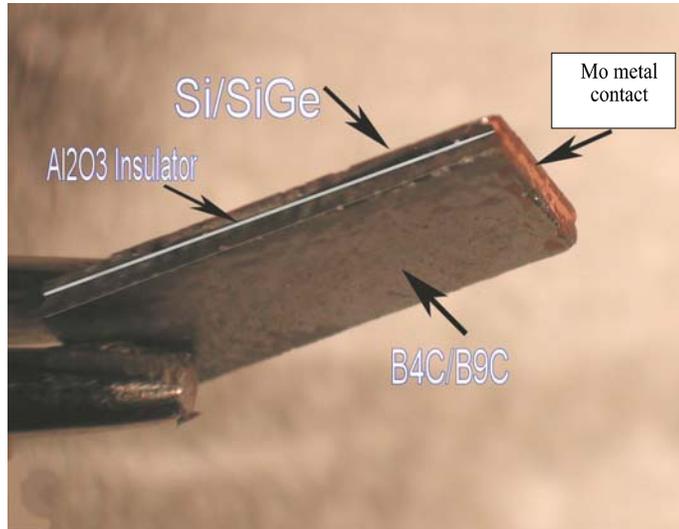


Figure 4. QW Si/SiGe-B₄C/B₉C couple for thermal stability test. The Mo was deposited by an improved sputtering process to obtain a lower contact resistance. An Al₂O₃ insulator was used to electrically separate the N & P legs. The power output is within a few percent of the expected calculated values.

The latest achievement in fabricating a two couple module helps meet the goal of depositing the QW films on Kapton and then joining the N and P legs with Mo contacts. Hi-Z's other high efficiency quantum well programs will also benefit from the materials and processes developed for this couple. The next step is to define and establish acceptable quantum well fabrication variables to produce a scalable and repeatable recipe for the Navy mW sensor power supply and the Army/DOE waste heat recovery programs.

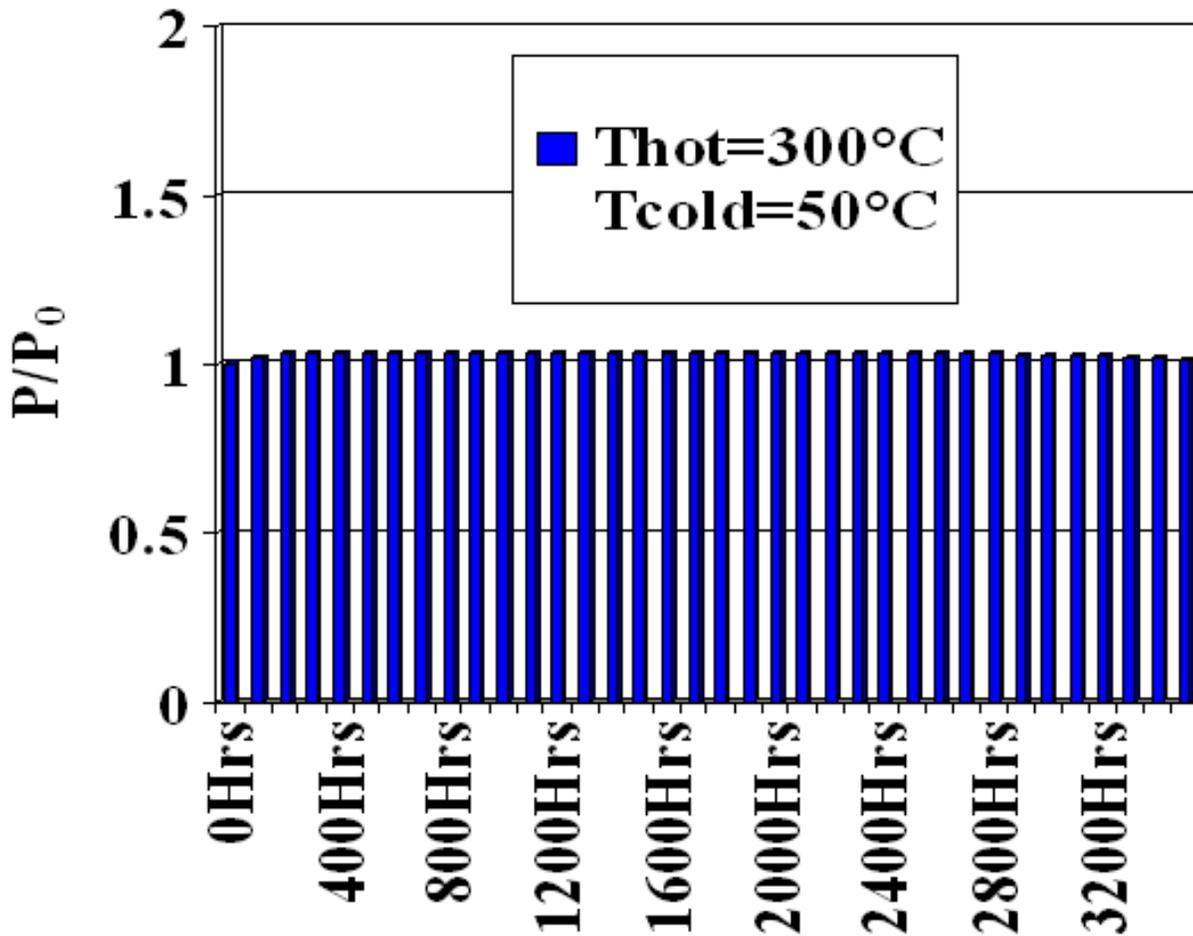


Figure 5. Power ratio life test data.

5 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. Ghamaty, S., Elsner, N., Wang, K. and Ziang, Q., "Thermoelectric Performance of B4C/B9C Heterostructures", Proceedings, 15th International Conference on Thermoelectrics, Pasadena, California, 1996.
3. Hicks, L.D., Dresselhaus, M.S., "Effect of Quantum-Well Structures on the Thermoelectric Figure of Merit," Phys. Rev. B. 47, 19 12 727-731, 1993.
4. Elsner, N.b., Ghamaty, S., Norman, .H., Farmer, J.C., Foreman, R.J. Summers, L.J., Olsen, M.L., Thompson, P.O. and Wang, K., "Thermoelectric Performance of Si0.8Ge0.2/Si Heterostructures by MBE and Sputtering", Proceedings, 13th International Conference on Thermoelectrics, AIP Press, Kansas, City. MO, 1994.
5. Elsner, N. B., "Review of PbTe Fabrication Techniques," MRS, Vol. 234.

6. Martin, P.M. and Olsen, L.C., "Scale-up of Si/Si_{0.8}Ge_{0.2} and Br₄C/B₉C Superlattices for Harvesting of Waste Heat in Diesel Engines", Proceedings 9th DEER Conference, Newport, RI, 2003.
7. Ghamaty, S, Elsner, N.B., Hi-Z Technology, Inc., U.S. Patent 6,096,965, "Quantum Well Thermoelectric Material on Organic Substrate", issued August 1, 2000.
8. Bass, J.C., Allen, D. T., Elsner, N.B., Hi-Z Technology, Inc., U.S. Patent 6,519,947, "Thermoelectric Module With Funneled Heat Flux," issued February 18, 2003.