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

QUARTERLY TECHNICAL PROGRESS REPORT

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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 and N-type Si/SiGe films on Kapton and Si substrate.

Gradient life testing are underway. One couple has achieved about 4000 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 QW Device on Kapton

During this period, Hi-Z has been studying the conditions present during the deposition of QW materials on Kapton in order to understand which of the important parameters used in the deposition process may be outside of the desired range, causing unexpectedly poor performance in the QWs that are created. The temperature of the Kapton substrate was directly measured before and during the sputtering process, and these measurements were compared with the controlled temperature of the substrate heater during previous and current deposition runs. A finite element thermal analysis was also performed on the heater and substrate assembly and compared with the measured substrate temperatures.

For the past few months, Hi-Z has been sputtering QW thermoelectrics onto Kapton substrates with two different geometries. Most recently, Hi-Z has been using a mask with 3 rectangular regions to sputter QW material for an expected efficiency test of these thermoelectrics. The mask, shown in Figure 1, leaves 3 regions of exposed Kapton that are each 0.5cm by 1.5cm. Once these strips have been successfully sputtered with QW thermoelectric layers, the strips can be cut out from the surrounding Kapton and stacked together for use in the efficiency test. The previous mask, used for depositing a radial module with 26 thermoelectric legs, is shown in Figure 2. The model shown differs slightly from the actual mask used. In the model, the legs are shown parallel to the radial direction from the center of the mask, but in the mask that was used for sputtering, the legs were angled slightly in a spiral pattern originating from the center. This spiral pattern of deposited QW films on a Kapton substrate can be seen in Figure 3. The reason for the

spiral design was so that the tip of one N-type QW leg could be electrically connected with the tip of another leg on the opposite side of the Kapton (P-type, spiraling in the opposite direction) and by connecting all of the legs in series, a continuous thermoelectric circuit could be created, zigzagging around the circumference of the module (see Figure 3).

Figure 1 – Three Strip Mask

Figure 2 – Mask for Module with 26 Legs

The modeled mask with straight radial legs was assumed to perform similarly to the actual mask in the thermal system studied because it had the same area of exposed Kapton in an almost identical geometrical pattern. Because the differences in geometries were so small, it is assumed that the errors caused by the difference in geometry are negligible.

Figure 3 – 26 Couple Radial QW Module before Kapton is Cut Away from the Inner and Outer Edges. Hi-Z has successfully fabricated QW modules with this geometry.

In both arrangements used for sputtering, identical masks were used on both sides of the Kapton and the masks were held against the Kapton by clamping them together between two stainless steel rings. This design allowed Hi-Z to flip the Kapton substrates and sputter QWs in the desired arrangement on both sides of the Kapton. The clamped Kapton substrate assembly was held against the substrate heater by four screws (not shown) with washers spaced around the outer edge of the heater. Since the substrate heater had a raised edge along the outer circumference, only ~0.05 inches of width around the outer edge of the clamped substrate assembly was held in contact with the heater. During sputtering of QW layers, the substrate heater was maintained at 325°C. In both thermal models used to analyze the Kapton substrates' temperatures, the heater ring in contact with the outer edge of the clamped assembly was held at 325°C and the back surface of the clamped assembly absorbed heat via radiation from the heater surface which was at 325°C. The clamped assembly dissipated heat via radiation from its outer surface to an environment at 30°C. The resulting temperature distributions of the clamped assembly and heater for the two types of masks are shown in Figures 4 and 5. In Figure 4 which shows the 3 strip mask, it can be seen that the temperature ranges greatly between the center and 2 outer exposed Kapton strips, and in the outer strips there is some significant variation in temperature as well. The temperature range shown is from 278°C to 325°C. In Figure 5, it can be seen that the regions where QWs are being deposited are a bit warmer and more uniform in temperature. The temperature ranges from 274°C to 325°C.

Model name: Small Sputtering Assembly - 3 Strip, No Deposition
Study name: Study 1
Plot type: Thermal Plot1
Time step: 1

Figure 4 – Temperature Distribution of Current 3 Strip Mask Assembly. Temperature Range is from 278°C to 325°C.

Model name: Radial Mask Analysis 2 - No QW Adjusted Scale
Study name: Study 1
Plot type: Thermal Plot1
Time step: 1

Figure 5 – Temperature Distribution of 26 Leg Mask Assembly (Used for Energy Harvesting Module). Temperature Range is from 274°C to 325°C.

Hi-Z believes that maintaining the proper substrate temperature during QW deposition leads to recrystallization and short range ordering of the initial silicon buffer layer. Once this buffer layer is properly fabricated, we feel confident that the QW structures deposited subsequently will be successful. Since the substrate temperature is an important factor in the success of the deposition

process, each of the sputtering masks (shown in Fig. 1 and 2) were modified to allow for the positioning of a small thermocouple between the mask and the Kapton substrate at the edge of one of the Kapton areas exposed during sputtering. When the substrate heater was raised to temperature (325°C) within the vacuum chamber, the measured temperature at the edge of the deposited substrate was significantly lower than the heater temperature (~100°C lower). Hi-Z believes that this large temperature gradient is caused by high thermal contact resistances within the vacuum chamber, especially between the substrate heater and the clamped substrate assembly. These thermal resistances within the vacuum chamber between the heater and the substrate may have been increased by the introduction of the thermocouple used to directly measure the temperature of the substrate (i.e. measured substrate temperatures may be lower than substrate temperatures in the system without the added thermocouple). Also, in any thermal calculations, the thermal contact resistances need to be estimated and input into the model. These estimated resistances can be a source for error within the model which may help to explain the large discrepancy between the calculated and measured temperatures between the heater and the substrate. In order to quickly compensate for the lower substrate temperatures measured within the vacuum chamber, we raised the heater set point temperature to a point where the measured substrate temperature was within the desired range. Using this method of heating the substrate, a few Kapton films were sputtered with silicon buffer layers and one Kapton film was deposited with QW structures. These completed films are currently being tested by Saeid to determine their properties.

Figure 6 – Schematic of Copper Piece Placed between Substrate Heater and Kapton Substrate Assembly to Provide Better Thermal Contact Between the Heater and the Substrate.

Once it was found that such a high temperature gradient existed between the substrate heater and the substrate, a parallel effort was begun to reduce the thermal resistance between the two. A new substrate clamping assembly was designed and fabricated (shown in Figure 6), allowing a piece of copper to be positioned between the heater and the clamped Kapton substrate. This copper piece

has a much larger contact area with the substrate heater and conducts heat to areas of the substrate that are in close proximity to the deposited areas. Figure 7(a) shows a design of the copper piece that will be in contact with the substrate heater, the substrate clamp, mask, and the region of the Kapton directly behind the deposited area. Figure 7(b) shows a design of the copper piece that will be in contact with the substrate heater, the substrate clamp, and the mask. The piece shown in Figure 7(b) and the other necessary substrate clamping components shown in Figure 6 have been fabricated and assembled.

Figure 7 – Copper Piece Used to Provide Thermal Contact Between Substrate Heater and Clamped Substrate Assembly. (a) Copper in Direct Contact with Kapton, Substrate Mask, and Substrate Clamp. (b) Copper in Direct Contact with Substrate Mask and Substrate Clamp.

The assembled heater with the new copper piece and clamping assembly is shown in Figures 8 and 9. The screw shown in the center is used to firmly attach all of the parts of the clamped Kapton assembly to the copper piece (holes for screws not shown in copper pieces in Figure 7). In the two photographs, the part of the clamped assembly shown on top has four holes around the edge which are used to attach and compress the entire assembly and the copper piece against the substrate heater. This top part was not included in the thermal analyses described in the following paragraphs because its design was not completed at the time the analyses were conducted.

A finite element thermal analysis of the new design (shown in Fig. 6) was conducted and the results are shown in Figure 10 (the copper piece shown in Fig. 3(b) used in the analysis) and Figure 11 (the copper piece shown in Fig. 3(a) used in the analysis). The analyses were conducted in a similar method to those shown in Figures 4 and 5 and described above.

Figure 8 – Picture of Copper Piece and Clamped Kapton Substrate Assembly on Substrate Heater

Figure 9 – Picture of Kapton Clamped in Place, Soon to be Placed in Vacuum Chamber.

However, in these analyses, there was no radiation heat input at the back of the clamped substrate assembly, and the central region of the back of the modeled heater was held at 325°C, whereas in the previous analyses (Fig. 4 and 5) the outer edge of the heater was held at 325°C.

Figure 10 – Analysis Results of Substrate Heater Assembly with Copper Piece in Contact with Substrate Clamp and Mask. Temperature Range is from 325°C to 307°C.

Model name: 2 Strip Mask with Copper Analysis 1 2006-05-22
Study name: Study 1
Plot type: Thermal Plot1
Time step: 1

Figure 11 – Analysis Results of Substrate Heater Assembly with Copper Piece in Contact with Kapton Substrate, Substrate Clamp, and Mask. Temperature Range is from 325°C to 307°C.

The results show that the region of the Kapton substrate where QW deposition will take place is only 5°C to 10°C below the set point temperature of the substrate heater. These results show that in the new design there is a considerable improvement in the thermal contact between the substrate heater and the substrate when compared with the previous design (Fig. 4 and 5).

4 QW Couples Fabrication with Mo Contacts on Si

An earlier single couple device that was fabricated with N-type Si/SiGe and P-type B_4C/B_9C , is shown in Figure 12. 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 4000 hours with no degradation (shown in Figure 13). The Si single crystal substrates have a high thermal conductivity and therefore are a major heat leak. Assuming bulk thermal- κ for the film the ZT of the couple without the Si substrate is calculated to be ~ 4 @25/C. To reduce this heat loss and increase efficiency, Kapton is being pursued in place of Si since its thermal κ is $\sim$ two orders of magnitude lower than Si. Kapton is also flexible, useful up to ~ 300 /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.

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 output is within a few percent of the expected 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 13. Power ratio life test data.

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