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THERMOELECTRIC QUANTUM WELL ENERGY HARVESTING DEVICE

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ABSTRACT

Hi-Z Technology, Inc., has recently fabricated a 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 metal contacts that exhibit a negligible contact resistance with both the N and P material. Initial measurements of power output from this Mo contacted device, from $T_{COLD} = 26$ to $T_{HOT} = 66^{\circ}C$, appear promising as they are close to the expected results of output power of 5 mWatts at 3 Volts for the complete device. The output voltage from this device was 225 mVolt, and total power was 0.371 mWatt at a temperature difference of $\sim 40^{\circ}C$. The power and output voltage of this device at the design $\Delta T = 40^{\circ}C$ are very close ($<10\%$) to the calculated values of the N and P materials. Extrapolating the two couple data to a full size device yields a total power of ~ 4.8 mWatt @ ~ 2.93 Volt for a complete 26 couple energy harvesting device enough power to operate a wireless sensor.

INTRODUCTION

QW materials are being developed at Hi-Z for a wide range of applications ranging in power levels from mW to kW. While the power levels are quite wide, the thermoelectric materials and the associated substrates on which the QW's are deposited remain the same and some of the joining techniques are also similar.

In this paper we address the fabrication techniques and logic of why they were selected for a mW power supply that is being developed for the U.S. Navy and many other users who need power supplies for their wireless sensors. The design methodology of this mW power supply was recently given by Jovanovic [1] of Hi-Z. The actual design is shown in Fig. 1 and uses a radial distribution of the N and P legs in which the waste heat from any source can be utilized such as a steam line or the surface of some operating piece of equipment. Designs are also being developed for using fossil fuels as well as isotopic heat sources

BACKGROUND

Hi-Z has measured α , ρ and κ thermoelectric properties of these QW materials and their ZT are shown in Fig. 2 for the QW material Si/SiGe.

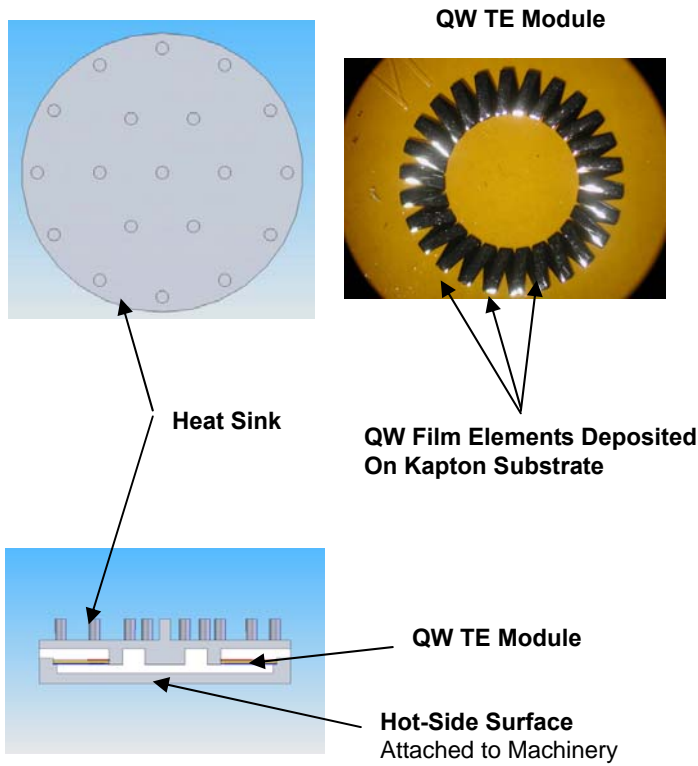


Fig. 1. Prototype Design of Energy-Harvesting QW TEG System

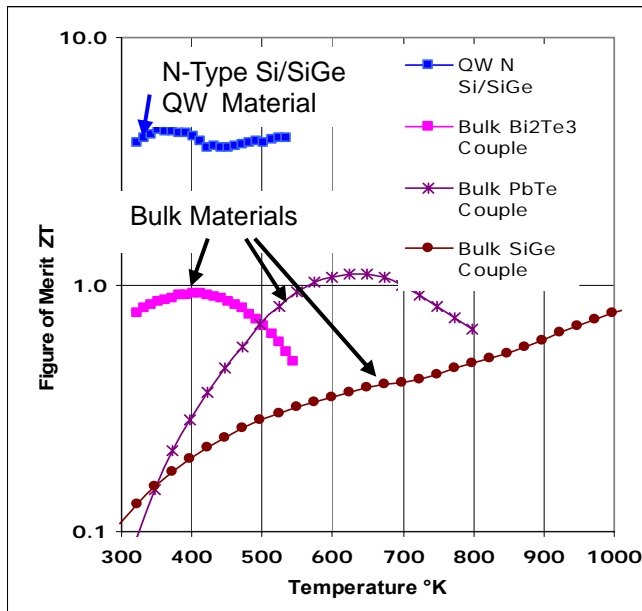


Fig. 2. Comparison of N-type Si/SiGe Quantum Well using measured α and ρ and published bulk κ (high κ to give conservative ZT) versus current Bi₂Te₃, PbTe and SiGe bulk thermoelectric alloys

To reduce the parasitic heat loss with the highly conducting Si substrate, Kapton™ was considered as a substrate material since its κ is an order of magnitude lower than Si, it is flexible and since its κ is so low, commercially available thicknesses of 1-5 mils can be used. To understand the importance of its use as a substrate, an analysis of a thermoelectric system utilizing Si, SiGe and a Kapton™ substrate was conducted and the results are shown in Fig. 3. As can be seen Kapton™ offers a 10% increase in absolute efficiency over a Si substrate. The drawbacks to using Kapton™ are its high CTE of 20×10^{-6} in/in/°C versus 4 to 5×10^{-6} in/in/°C for Si and Ge and its restricted temperature of operation during sputter deposition of $\sim 350^\circ\text{C}$. Further, if Kapton™ is to be used as a substrate it must be coated on both sides to balance out the differences in its CTE with the Si and SiGe alloys.

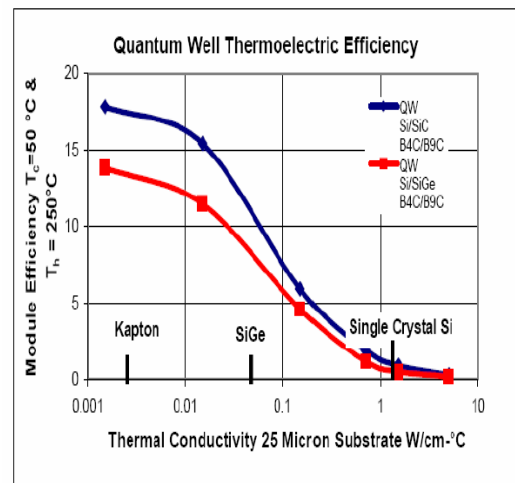
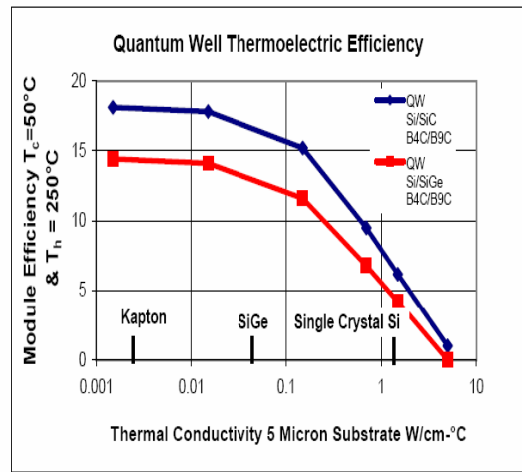
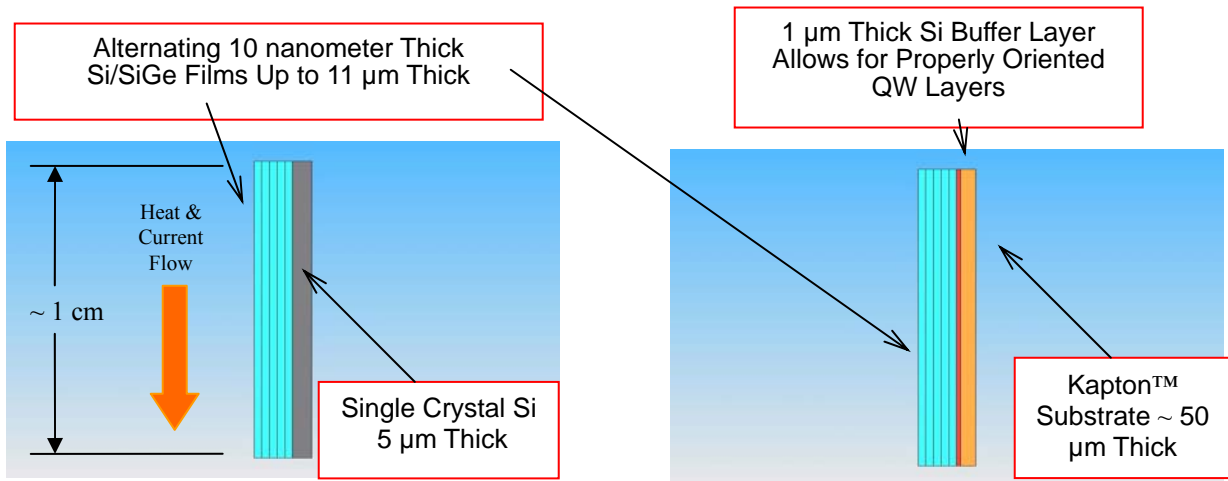


Fig. 3. QW Thermoelectric System Efficiency as a Function of Substrate Thermal Conductivity

The Kapton™ upper limitation of 350°C is restrictive to depositing the 1 μm thick Si buffer coat. It is desirable that the Si buffer coat exhibit a crystalline structure or short range ordering of its structure, and in this condition it is readily achieved with Si substrates. In this condition the subsequent Si/SiGe QWs will deposit and grow to yield the favorable QW thermoelectric properties. With Kapton™ this condition is

more difficult to achieve. Studies are in progress to characterize and verify that this desired buffer layer will be routinely produced. A comparison of the deposition parameters between the initial QW demonstration using single crystal Si substrates and the presently used parameters being pursued with Kapton™ are shown in Fig. 4.



- Initial Concept and Demonstration**
- Yielded 14% efficiency at a T_H of 250°C, T_C 50°C when used as N leg and P leg was B_4C/B_9C
 - Single crystal Si has too high a thermal conductivity
 - Polycrystalline Si or SiGe thermal K, 10X lower
 - Parasitic heat loss > 50% because of single crystal Si
 - Biggest gain to be made is to reduce the thermal K of the substrate

- Fabrication Approach for $T_H < 300^\circ C$**
- Kapton™ is flexible and has very low thermal conductivity. Alternates are glass and SiGe
 - Si buffer layer is deposited to allow the Si/SiGe to achieve proper orientation
 - SiGe can replace Si as the buffer layer and further lower parasitic heat losses
 - Parasitic heat losses estimated at ~5%
 - Results with Kapton™ promising

Quantum Well Coating Approach

- QW materials must be alternately deposited at 10 nanometer intervals on some substrate.
- A lower thermal conductivity substrate is used to deposit the QWs since the heat will flow in parallel through the QW films and the substrate, therefore
- The ratio of QW thickness to substrate's thickness needs to be maximized to minimize heat flow
- Since sputtering of QW films is slow and expensive, the incentive is to minimize the number of QW films required, which in turn requires the substrate thickness to be minimized.

Fig. 4. Comparison of Initial concept With Si Substrate and Concept With the Low Thermal Conductivity Kapton™ Substrate for Quantum Well Films and QW Coating Approach

The original selection of Mo, as the contact material, was based on the work of Sweet [2] who investigated Mo and W contacts for SiGe milliwatt generators for Sandia applications to operate at a T_H of $\sim 450^\circ\text{C}$. W sputter contacts were developed that lasted for 10 years. Mo was also rated acceptable for this application. Mo was initially evaluated by Hi-Z in fabricating a prior QW couple composed of N type Si/SiGe and P type B_4C/B_9C (Fig. 5). This couple is presently operating at a T_H of 300°C and has achieved over 4,000 hours with fairly stable performance (Fig. 6) but might be beginning to degrade, and if so less reactive W will be pursued. Mo was selected because its CTE is between the CTE of Si/SiGe and B_4C/B_9C and it is more ductile than W. Based on the favorable performance of Mo with this first couple, Mo was selected for the contacts for the two Si/SiGe radial couples shown in Fig. 7.

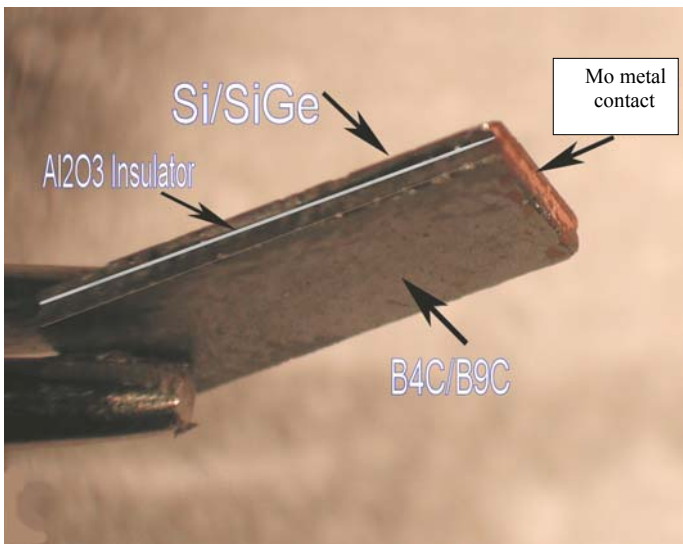


Fig. 5. QW Si/SiGe- B_4C/B_9C Couple for Thermal stability Test. The Mo was deposited by an improved sputtering process to obtain a lower contact resistance. An Al_2O_3 insulator was used to electrically separate the N and P legs. The power output is within a few percent of the expected calculated values.

From the work of Reference 2 and the multi year SiGe bonding program by RCA [3], the wear out mechanism with either Mo or W with SiGe alloys is the progressive silicide formation at the interface. The silicide formation causes an increase in volume with an accompanying increase in contact resistance and eventual failure. For higher operating temperatures $>300^\circ\text{C}$ where KaptonTM is unacceptable and Mo and W degrade, the Si-15Mo alloy contacts, developed by RCA for the bulk SiGe alloys, have shown low contact resistances and will be used with the QW films since they have been operating near 1000°C with stable performance on the Voyager I and II spacecraft since 1977.

EXPERIMENTAL PROGRAM

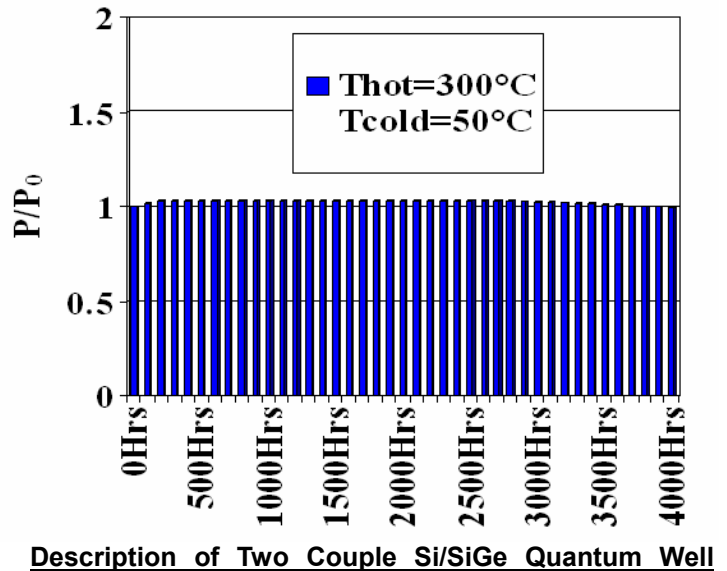


Fig. 6. Power Ratio Life Test Data

Device

Figure 7 shows a QW device with two couples of N and P-type Si/SiGe deposited on both sides of a KaptonTM substrate. 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. A sputtering process was successfully developed to deposit the Mo metal contacts that exhibit a negligible contact resistance with both the N and P material.

The 26-couple device was fabricated by sputter deposition of a $1\ \mu\text{m}$ thick Si buffer layer followed by (without breaking vacuum) 800 layers of 100\AA thick alternating Si and SiGe layers on each side of the KaptonTM substrate.

Subsequent examination of the film by Auger analysis indicates it is crystalline and/or exhibits short range order.

These films are too thin to be characterized by conventional x-ray diffraction and techniques such as low angle surface glancing x-ray analysis, Raman scattering and electron diffraction are being pursued for further characterization. Thus far Auger analysis has been the only technique that can be routinely used to distinguish crystallinity or short range order as shown in the examples in Figs. 8 and 9.

A stainless steel mask was used to deposit the radial layout shown in Fig. 7.

A separate sputter system was used for the deposition of the Mo contacts. It was not possible to rotate the KaptonTM disc, therefore only two couples were coated. The amount

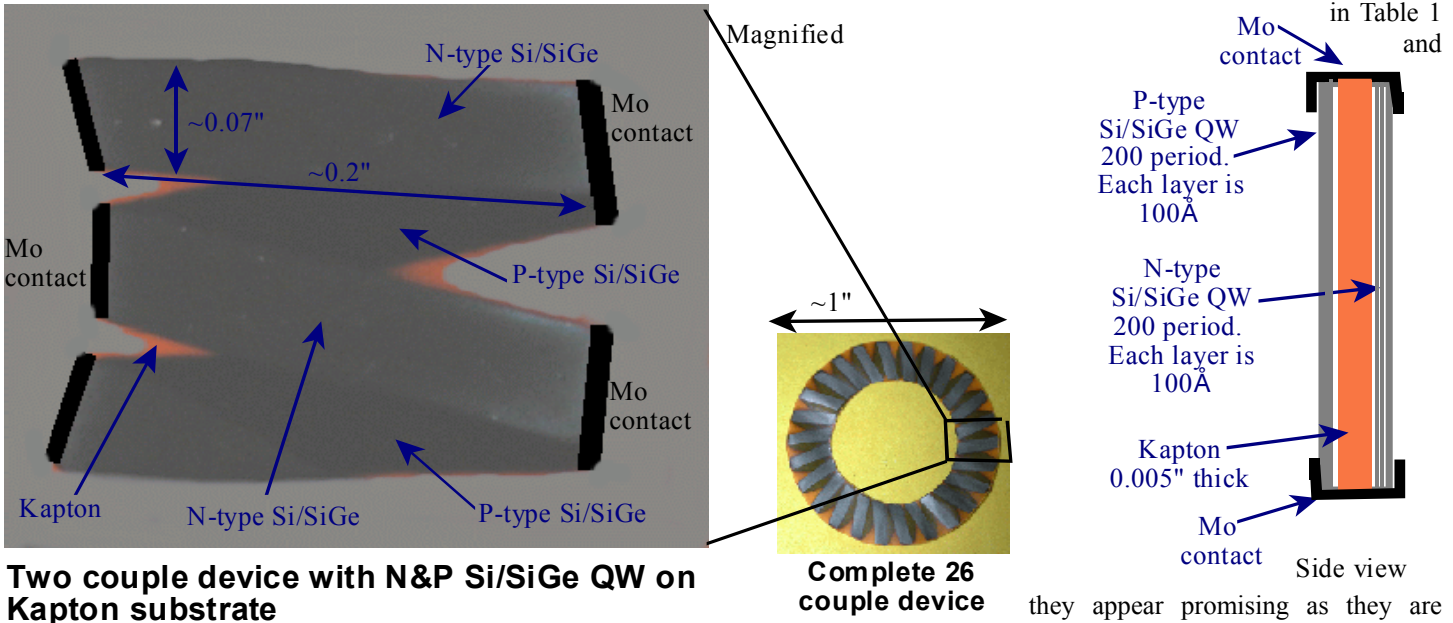


Fig. 7. QW N- and P-Type Si/SiGe Two Couple Device on Kapton™. The Mo was deposited by an improved sputtering process yielding the first QW device on Kapton™.

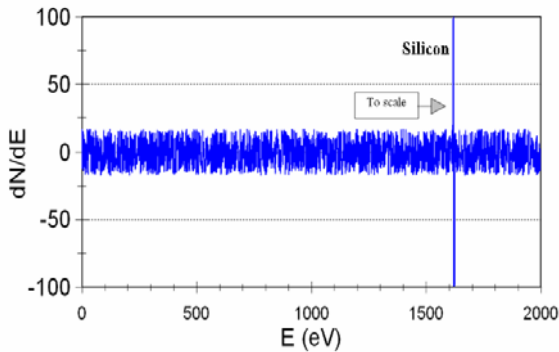


Fig. 8. Auger Emission Spectroscopy (AES) of a Bad Film Deposited at ~325°C on Kapton™. The resistivity of this film is very high (>1 Ohm-cm). The AES of the Si Buffer layer is shown. The large noise (the oscillations in the count) is an indication of the amorphous structure.

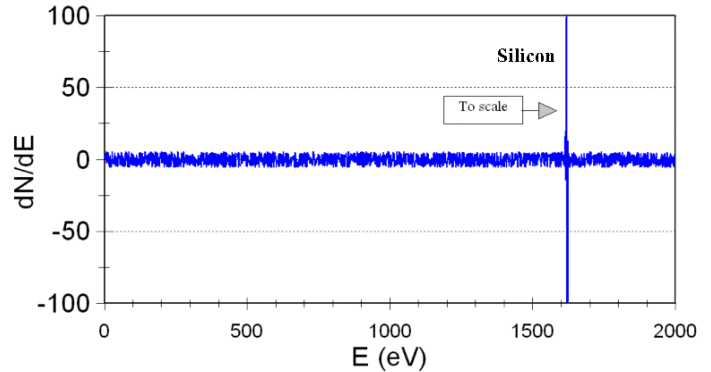


Fig. 9. Auger Emission Spectroscopy (AES) of a Good Film Deposited at ~325°C. The resistivity of this film is ~1 Ohm-cm. The AES of the Si Buffer layer is shown. The small noise (the oscillations in the count) is an indication of the near neighbor structure in the film.

of Mo is estimated at 10 μms and was deposited so it is thought to be bonded to every 100Å thick layer and was extended around the corners as shown in Fig. 7 to provide maximum contact area.

RESULTS AND DISCUSSION

Two Couple Device with Si/SiGe QW and Mo Contacts on Kapton Substrate Yields Expected Power

Initial measurements of power output from this Mo contacted device, from T_{COLD} = 26 to T_{HOT} = 66°C, are shown in Table 2, and the results

Table 1. Thermoelectric Properties of QW Device on Kapton™ with Mo Contact Compared to Calculated Values

Each N and P leg is 200 periods of Si/SiGe, and each layer is 100 Å thick (total 4 μm). Each legs area is ~0.07 in. x 0.2 in. The Kapton™ is 0.005 in. 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 $\Delta T = 40^{\circ}\text{C}$	Results 2 Couples Measurements Extrapolated to 26 Couples at $\Delta T = 40^{\circ}\text{C}$	26 Couples at $\Delta T = 40^{\circ}\text{C}$	
			QW with ZT ~ 3.0	Bulk $(\text{Bi,Sb})_2(\text{Se,Te})_3$ with ZT ~ 0.75
Voltage (VOC)	225 milli V	2.93 V	3 V	0.5 V
Power	0.371 milliWatt	4.82 milliWatt	5 milliWatt	1.5 milliWatt



Fig. 10. Photomicrograph of N and P Si/SiGe Quantum Well Module During Fabrication with a Stainless Steel Mask: N-type Deposited on One Side of Kapton™ and P-type on the Opposite Side

From an efficiency standpoint, the following has been calculated using the measured power data.

Assuming known 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% @ $\Delta T = 40^{\circ}\text{C}$. 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% @ $\Delta T = 40^{\circ}\text{C}$ with no allowance for a substrate; with a substrate, the ZT and efficiency values would be even lower.

QW films, however, typically have a thermal conductivity ~1/3 of their bulk values [4, 5]. Therefore the efficiencies we expect with the QWs should be even higher than the conservative numbers given in Table 1.

It is planned to perform thermal aging of this device, and similar devices with metal contacts, such as Mo or other materials, and life test 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 (an ion plater) is being upgraded so we may complete the milliWatt device and fabricate multiWatt modules for the DOE and Army programs.

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. 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 criteria to produce a scalable and repeatable recipe for all power levels for the Navy mW sensor power supply and the Army/DOE waste heat recovery programs.

CONCLUSIONS

1. Kapton™, a very low thermal conductivity organic film, can be used as a substrate to deposit Quantum Well films. Substrates such as Si do not appear necessary for low temperature operation.
2. Low resistance electrical contacts can be obtained between Mo and Si/SiGe QW materials.
3. Si/SiGe QW films deposited on Kapton™ yielded the expected (within 10%) resistance, voltage and power on a two couple module device.

4. Further characterization and upgrading of the films is underway to allow repeatable deposition for larger area samples.

NOMENCLATURE

α	Seebeck coefficient
ρ	Electrical resistivity
κ	Thermal conductivity
ZT	Figure of merit
QW	Quantum Well

ACKNOWLEDGMENTS

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