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HIGH COEFFICIENT OF PERFORMANCE QUANTUM WELL THERMOELECTRIC NANO COOLER

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ABSTRACT

Nanotechnology quantum well thermoelectric materials have been developed that have high Figures of Merit and that can attain very high coefficients of performance (COP) to satisfy the requirements for cooling room temperature detectors. Hi-Z Technology, Inc. (Hi-Z) has developed Si/SiGe solid state quantum well (QW) thermoelectric (TE) materials that have demonstrated a Seebeck coefficient and thermoelectric properties that provide >4X higher conversion efficiencies than the current bulk TE materials. With the new Si/SiGe QW materials, cooling systems can be designed that are much smaller, quieter, lighter weight, and that have much reduced power requirements than current TE materials or presently used vapor-compression systems. On-going development for these new QW TE materials has demonstrated high-efficiency TE materials for power generation applications ranging from providing power for wireless sensors to converting waste heat from diesel engine exhaust directly to electricity and thus reducing the load on the alternator and reducing fuel consumption. Now, cooling devices with a high coefficient of performance (COP) are feasible and are being designed for room temperature detector cooling applications. Multi-layer nanocomposite QW films (each 10 nm thick) were fabricated to demonstrate that Si/SiGe QW materials can be deposited on a low thermal conductivity substrate and provide at least the desired COP over the required temperature range of 250K to 350K in a single-stage nano cooler. These QW thermoelectric materials can also be implemented into commercial equipment in the air conditioning and refrigeration applications, thus eliminating fluids, ozone-impacting refrigerants and compressors. Thermoelectric properties of QW thin-film materials have been measured at Hi-Z, several universities and national labs. The conversion efficiency of QW materials has been measured at Hi-Z in two different test couples and in a two-couple device. In all cases, good agreement was obtained between the measurements and prior analytical predictions. Cooling

performance was measured in a test with one QW TE element and good agreement was obtained between measurements and analytical predictions. TE properties of the Si/SiGe QW material used in the analysis and design of the subject TE nano cooler were recently independently verified at University of California San Diego (UCSD) and the U.S. National Institute of Standards and Technology (NIST). This paper deals with the analysis of a high COP QW TE single-stage nano cooler for room temperature detectors and with the improved TE properties obtained with the QW thin-film materials resulting in such high COP designs.

INTRODUCTION

New imaging systems being developed for the U.S. Army require cooling systems that can attain very high COPs, that are low consumers of battery power, that are of small size and weight, and that have no moving parts. In particular, a COP greater than 0.3 at 280K against an ambient temperature of 350K (including heat sink rise) and a COP greater than 0.1 at 250K against the same heat sink temperature are being sought. These goals are beyond the capabilities of the state of the art (SOTA) bulk TE coolers. This paper deals with the application of the innovative QW TE technology to a nano cooler design that could satisfy the above goals.

NOMENCLATURE

T	temperature (K), or (C)
V	DC voltage (v)
Z	thermoelectric figure of merit (K^{-1})
Å	Angstrom
in	inch
η	thermoelectric efficiency
α	Seebeck coefficient (K/V)
κ	thermal conductivity (W/cm-K)
ρ	electrical resistivity (Ω -cm)

Summary of Quantum Well Thermoelectric Technology

A summary of the Quantum Well thermoelectric technology is provided in this section. Ghamaty [1] provides a more detailed discussion. New QW thermoelectric materials are being developed that are expected to yield conversion efficiencies several times that of present day bulk materials. A comparison of latest and previous results is shown in Figure 1 illustrating time history of the dimensionless figure of merit, ZT, which is a measure of performance. For over 35 years, the ZT stayed close to the value of 1. However, recent breakthroughs have occurred in the figure of merit by using the QW alternatives to bulk material, with the QW material reaching the remarkable ZT value of 4.1 in recent tests. This value corresponds to a conversion efficiency of 14%, which was measured in tests in October 2002. This high efficiency has been reconfirmed in separate tests completed in May 2003 as shown in Figure 2. It is this breakthrough that allows QW TEGs to meet the goals of this study. Based on the current experimental work, thermal to electric conversion efficiencies of 20-40% at a T_H of 250°C to 700°C and a T_C of 50 to 100°C are anticipated.

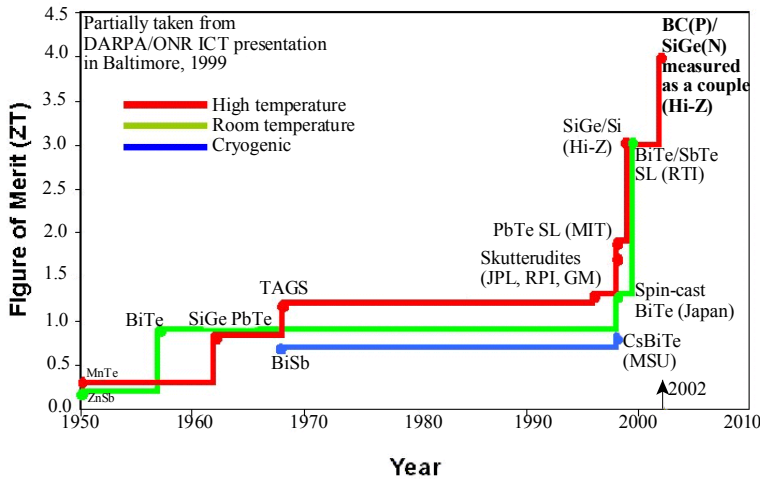


Fig. 1 History of Thermoelectric Dimensionless Figure of Merit, ZT, (partially taken from Ref. 2)

Thermoelectric materials are presently used for power generation in remote locations, for example in deep space probes. Usage in a wider range of applications is conditional upon improvement in the efficiency of energy conversion from heat into electricity and in the specific cost of power generation (\$/W). The efficiency of thermoelectric energy conversion devices is strongly limited by the performance of the materials, which is normally measured in terms of a *Figure of Merit Z*.

The thermodynamic efficiency, η , of a thermoelectric power generator is given by

$$\eta = \left\{ \left(\frac{T_h - T_c}{T_h} \right) * \left\{ \frac{M - 1}{M + T_c / T_h} \right\} \right\}, \quad (1)$$

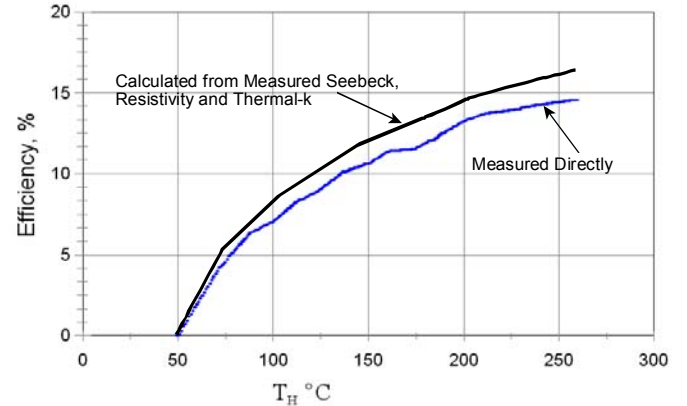


Fig. 2 Measured and Calculated Efficiency (P_{out}/P_{in}) of QW B_4C/B_9C -Si/SiGe Couple versus Hot-Side Temperature from Power Data Measured in Tests in May 2003

where the first term in brackets is the Carnot efficiency and the remaining terms are thermoelectric factors with M defined by

$$M = \left\{ 1 + Z(T_c + T_h) / 2 \right\}^{1/2}, \quad (2)$$

with T_h and T_c the temperature of the hot and cold junctions respectively. To achieve a high efficiency, the thermoelectric figure of merit Z must be high. For a specific material,

$$Z = \alpha^2 / \rho(\kappa_L + \kappa_e), \quad (3)$$

where ρ is the electrical resistivity, α is the Seebeck coefficient, κ_L is the lattice or phonon contribution to the thermal conductivity and κ_e is the electron contribution to the thermal conductivity. Much of the effort to improve Z over the last 20-30 years has been focused on attempts to reduce the lattice thermal conductivity without affecting the electrical resistivity. Solid solution alloying, as in the case of silicon-germanium, has been effective in this respect; also the search for new materials with structures favorable for poor phonon propagation has led to several promising candidates such as the skutterudites [3].

The breakthrough approach to increasing Z is to form compositionally modulated materials, mainly by QW confinement of carriers in the active layers in a multilayer film by the adjacent barrier layers. The core concept is to enclose each electrically active layer by a material that has a band offset sufficient to form a barrier for the charge carriers. The major improvement in Z is expected to follow from an increased Seebeck coefficient which results from an increase in the density of states. The electrical resistivity ρ decreases due to a large increase in the mobility of the carriers and the thermal conductivity κ is reduced due to strain between the

QW and barrier layers, which in turn inhibit phonon flow. QW effects become significant only when the thickness of the active layer is small, below approximately 200Å.

Theoretical models predict that values of ZT of 2 and above are possible in a variety of low-dimensional structures, but only the B₄C/B₉C and Si/SiGe have demonstrated performance above this level to date, i.e., a ZT of ~4. It appears that Si/SiGe, Si/SiC and B₄C/B₉C QW layers can be economically and reliably sputtered on Si substrates. Si/SiGe QW layers have also been sputtered on Kapton substrates.

Thermal conductivities of Si/SiGe quantum well films were measured with the 3ω-method. Values obtained by this technique indicate a large decrease (factor of 3) in κ_{in-plane} for the Si/SiGe quantum wells versus the bulk material and this is in agreement with theory. Under the U.S. Department of Energy funding, the first data was generated that indicated that the multi-layer QW films of alternating layers of Si and SiGe have a figure-of-merit that is more than an order of magnitude higher than bulk SiGe near room temperature and below. These films were grown by the molecular beam epitaxy (MBE) and by sputtering. Ghamaty [1] and [4] and Bass [5] and [6] describe recent progress in the development of high efficiency QW thermoelectrics.

PREDICTED PERFORMANCE FOR NANO COOLER

Presently used bulk thermoelectric materials exhibit a ZT of <1 and as shown in Figure 3 quantum well materials properties indicate ZT >>1. Current Bi₂Te₃ based alloys are not competitive with conventional vapor compression equipment and in applications, such as room temperature detectors and night vision goggles, are large consumers of batteries.

However, QW materials are emerging with much higher ZTs (Fig. 3) and potentially much higher COPs as shown in Figure 4. With these new Si/SiGe QW materials, cooling systems can be fabricated that are much smaller, quieter, lighter weight, and have much reduced power requirements than the presently used mechanical equipment. The very encouraging thermoelectric data presented appear to show that QW materials when fully developed can meet the many demanding Army cooling applications and these accomplishments can also be implemented into commercial equipment for the air conditioning and refrigeration markets. A comparison of cooling performance of the QW and SOTA bulk thermoelectrics and current mechanical vapor compression cycles is shown in Figure 5. This figure illustrates that QW thermoelectrics have large COPs that can compete with mechanical vapor compression systems.

Using the measured Seebeck coefficient of 955 μV/K and a measured electrical resistivity of 0.99 mΩ-cm, the QW nano

cooler is predicted to pump 14 Watts from the cold side at T_H = 350K and T_C = 250K. Each quantum well element contains 11 micron layers composed of alternating 100 Å Si and 100 Å SiGe films. Each 11 micron layer is deposited on a 25 micron Kapton substrate. Commercial Bi₂Te₃ modules will not pump heat away from the cold side at this 100K temperature

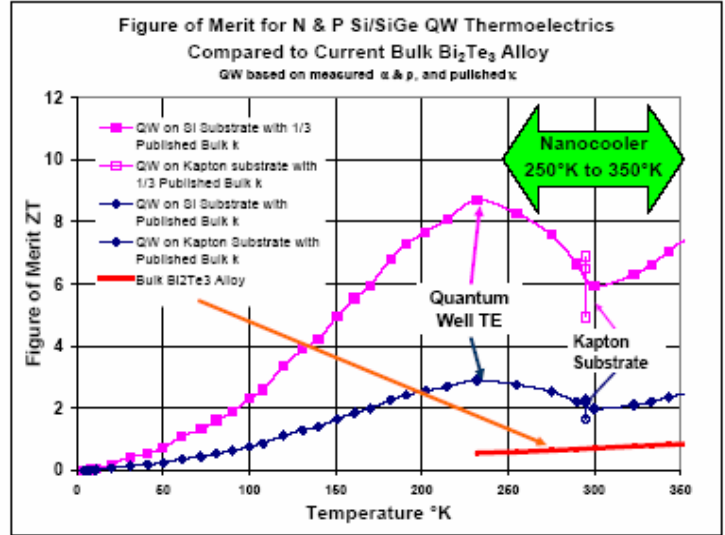


Figure 3. Dimensionless Figure of Merit for N and P Si/SiGe QW Thermoelectrics Compared to Current Bulk Bi₂Te₃ Alloy.

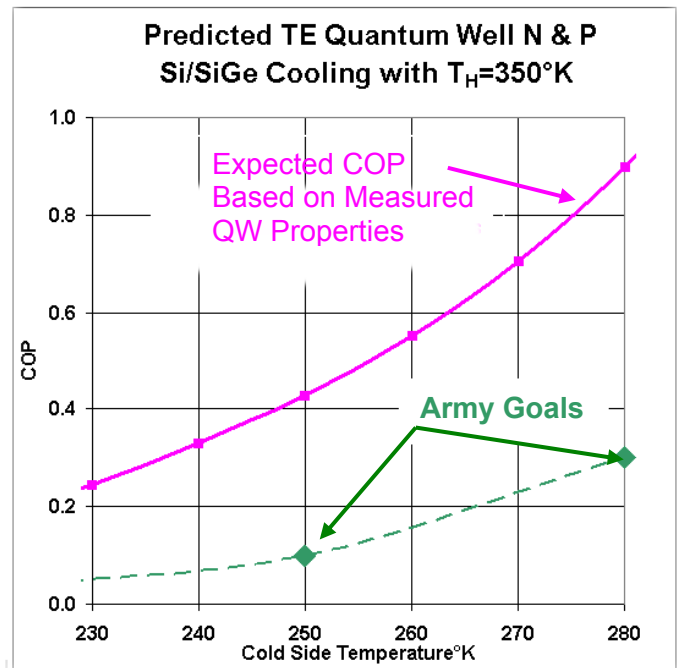


Figure 4. Predicted Performance of a Single Stage Quantum Well Cooler Based on Measured Seebeck Coefficient, α, and Electrical Resistivity, ρ over this Temperature Range and the Most Conservative Published Bulk Thermal Conductivity, κ

difference since the COP is less than zero, and electricity will generate heat that is dissipated at both the hot and cold junctions. In contrast, the QW thermoelectrics will remove

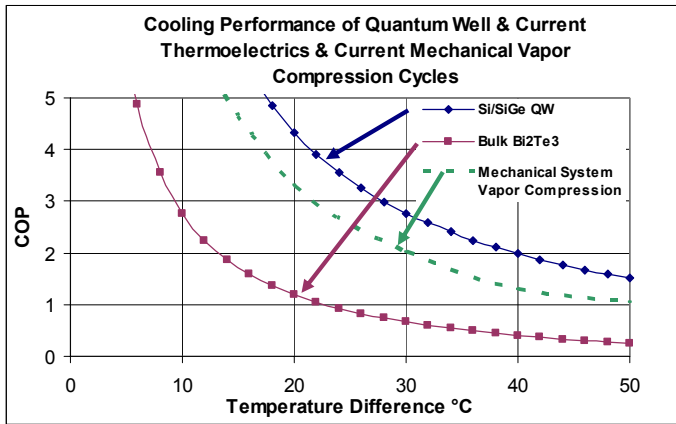


Figure 5. COP of QW and Current Thermoelectrics and Current Mechanical Vapor Compression Systems

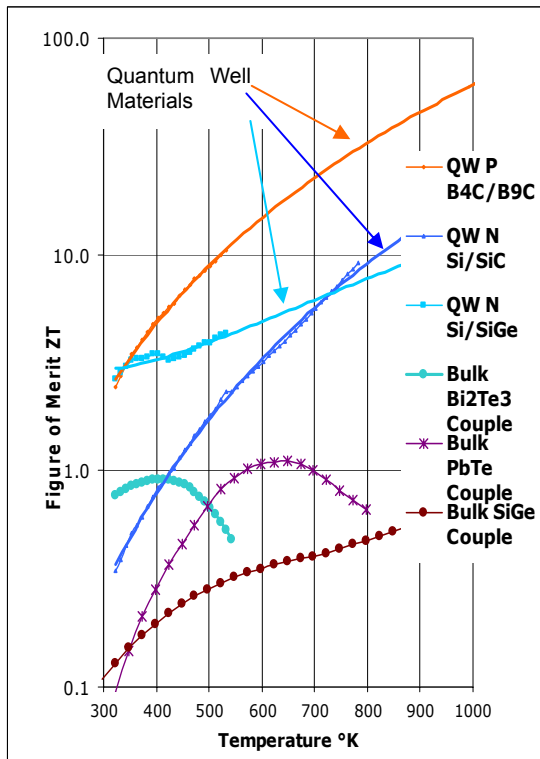


Figure 6. Quantum Well Thermoelectrics have an Order of Magnitude Improvement in Thermoelectric Dimensionless Figure of Merit Compared to Other Current Materials and Improve at Higher Temperatures. For QW Si/SiGe material, thermal conductivity decreases with temperature and this effect is included in ZT values. For nano cooler temperatures, Si/SiGe quantum well films have superior performance as shown in Figure 4.

heat with a COP of 0.43 at a 100K temperature difference. With QW thermoelectrics heat will be removed up to a temperature difference of 165K.

Hi-Z is currently evaluating several different substrates for the deposition of the QWs with the goal of selecting the one(s) which yield repeatable QW properties that have sufficiently low thermal conductivities and can reach the COPs shown in Figure 4. The choice of substrate material is crucial since it is a parasitic heat leak which is to be minimized, yet it is the necessary platform from which the films are deposited. Hi-Z is taking a unique approach with heat flow and current flow parallel to the direction of the alternating 10 nanometer thick Si/SiGe films. Another approach for cooling is to have heat and current flow normal to the film as widely reported (References 7 to 14) and improvements over bulk alloys have been demonstrated. However, Hi-Z's approach gives much higher Seebeck coefficients (4X) and higher ZT's (3X) as shown in Figures 3 and 6.

Limited film thicknesses and temperatures (~125C) are inherent when using the approach with heat and current flow normal to the superlattice film. Whereas, with heat and current parallel to the film, many thicknesses (*i.e.* heat flux boundary conditions) and very high temperatures are possible. This latter approach takes advantage of the quantum well effect in which the Seebeck coefficient is increased due to an increase in the density of states, the electrical conductivity is increased due to enhanced mobility of the carriers and thermal conductivity is reduced due to phonon scattering at the QW layer interfaces.

EXPERIMENTAL PROGRAM

QW TE Element Operated as a Cooler

In a Hi-Z experiment, the B₄C/B₉C film alone was used as a single element QW cooler, creating a maximum temperature difference of ~45K. This temperature difference gives a ZT of ~3 for T~25C. For this experiment, the P-type B₄C/B₉C was joined to a small Cu wire as shown in Figure 7. This test serves as another confirmation that the QW materials exhibit a much higher figure of merit than bulk alloys.

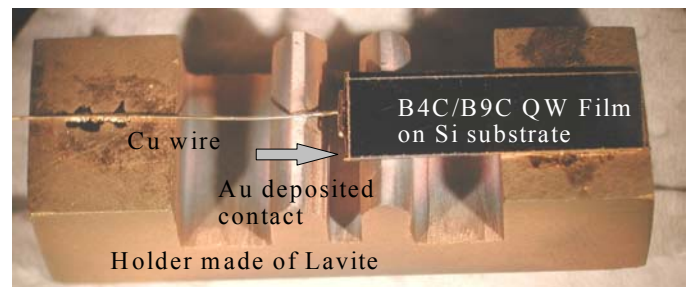


Figure 7. P-Type B₄C/B₉C QW Film Joined to a Copper Wire Operating as a Cooler

Two-Couple QW Device That Yielded Expected Power

Figure 8 shows a QW device with two couples of N and P-type Si/SiGe deposited on both sides of a Kapton™ 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 molybdenum metal contacts that exhibit a negligible contact resistance with both the N and P materials.

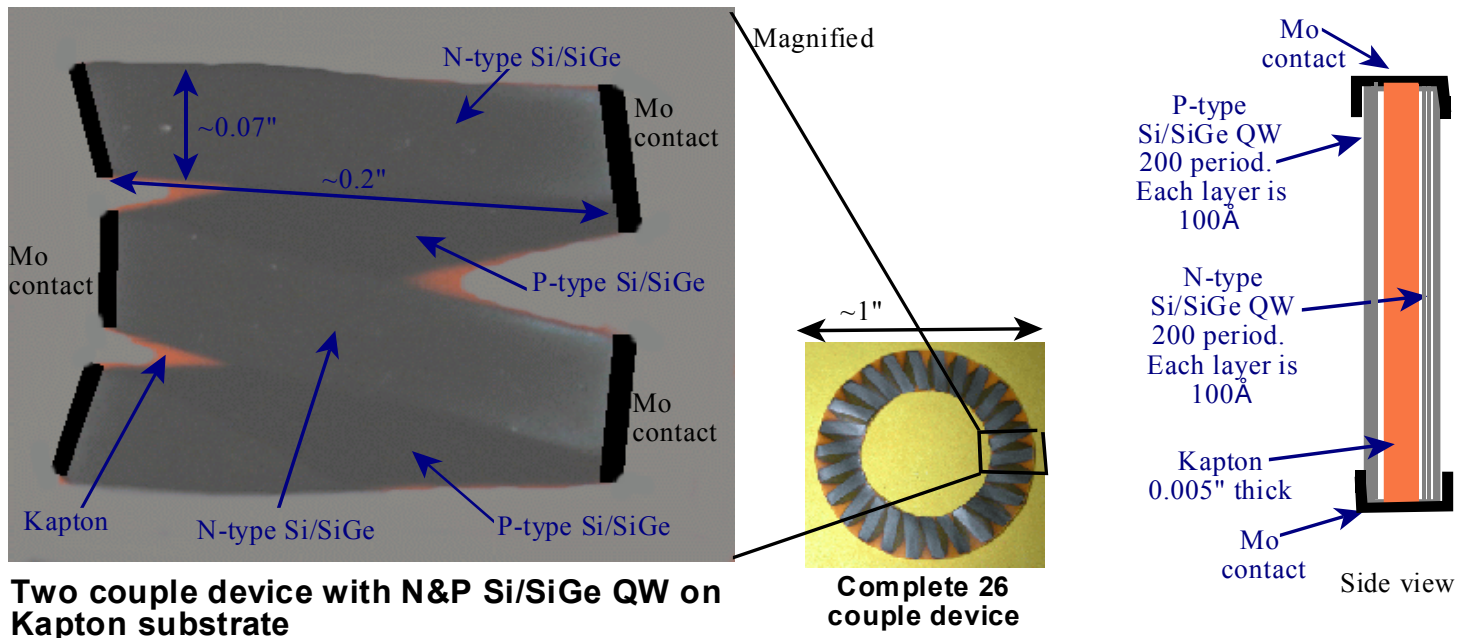


Fig. 8. QW N- and P-Type Si/SiGe Two Couple Device on Kapton™. The Mo was deposited by an improved sputtering process yielding the first QW device on Kapton™.

The 26-couple device was fabricated by sputter deposition of a 1 μm thick Si buffer layer followed by (without breaking vacuum) 400 layers of 100Å thick alternating Si and SiGe layers on each side of the Kapton™ substrate

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. A stainless steel mask was used to deposit the radial layout shown in Figure 8. Detailed description of this QW module design to provide power for wireless sensors is given by Jovanovic [15].

A separate sputter system was used for the deposition of the Mo contacts. It was not possible to rotate the Kapton™

disc, therefore only two couples were coated. The amount of Mo is estimated at 10 μm and was deposited so it is thought to be bonded to every 100Å thick layer and was extended around the corners as shown in Figure 8 to provide maximum contact area.

Initial measurements of power output from this Mo contacted device, from $T_{COLD} = 26C$ to $T_{HOT} = 66C$, are shown in Table 1 and they appear promising as they are close to the calculated results. The output voltage from this device was 225 mV, and total power was 0.371 mW at a temperature difference of 40C. The power and output voltage of this

device at the design $\Delta T = 40C$, 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 ~4.8 mW at ~2.93 V for a complete 26 couple energy harvesting device, enough to power a wireless sensor.

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

Assuming known literature bulk thermal conductivity of the Si/SiGe films for evaluating this device, the ZT is calculated to be ~3 at 25C, which yields an efficiency of ~3% at $\Delta T = 40C$. (This ZT value is somewhat higher than the values shown in Figures 3 and 6 due to the differences in the substrate materials and thicknesses and the QW film thicknesses.) In comparison, a Bi₂Te₃ device would have a ZT of ~0.75 to 1.0 at 25C and a maximum efficiency of ~1.5% at $\Delta T = 40C$ 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 $\sim\frac{1}{3}$ of their bulk values [16, 17]. Therefore the efficiencies we expect with the QWs should be even higher than the conservative numbers given in Table 1, and the predicted COPs given in Figures 4 and 5 should also be higher.

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. The next step is to define and establish acceptable quantum well fabrication criteria to produce a scalable and repeatable recipe for the Army nano cooler and other programs. It is also planned to test the two-couple device as a cooler.

QW properties at the Jet Propulsion Laboratory (JPL) and the Oak Ridge National Laboratory (ORNL). Thermal conductivity data for QW TE materials are also planned to be verified. It should be noted that a lower Seebeck coefficient and higher electrical resistivity and the published bulk thermal conductivity values were used in the analysis presented in this report and that the predicted COPs shown in Figures 4 and 5 are thus conservative.

CONCLUSIONS

Nanotechnology quantum well thermoelectric materials have been developed that have high Figures of Merit and that

Table 1. Thermoelectric Properties of QW Device on Kapton™ Substrate with Mo Contacts 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.

$T_{COLD} = 26^{\circ}C$ $T_{HOT} = 66^{\circ}C$	EXPERIMENTAL QW RESULTS		CALCULATED	
	2 Couples Measured at $\Delta T = 40^{\circ}C$	2 Couples Measurements Extrapolated to 26 Couples at $\Delta T = 40^{\circ}C$	26 Couples at $\Delta T = 40^{\circ}C$	
			QW with ZT ~ 3.0	Bulk $(Bi,Sb)_2(Se,Te)_3$ with ZT ~ 0.75
Voltage	225 mV	2.93 V	3 V	0.5 V
Power	0.371 mW	4.82 mW	5 mW	1.5 mW

Independent Verification of Si/SiGe QW TE Properties

The enhanced performance and high COPs predicted in this study are a direct function of the improved properties that are the result of the QW effects. It is very important that such QW properties can be repeatedly measured and independently verified. The first independent verification was recently performed by the UCSD Prof. Prabhakar Bandaru. He made his measurements of N and P Si/SiGe QW films (1 μm thick) deposited on a 500 μm Si substrate that were made in the same sputtering run as the samples characterized earlier by Hi-Z, and he obtained essentially the same results. His value for the Seebeck coefficient of 1300 μV/K is practically the same as Hi-Z's value of 1320 μV/K. For electrical resistivity, his mean value of ~ 0.4 mΩ-cm is somewhat lower than the Hi-Z value of ~ 1 mΩ-cm. After the InGa liquid metal contacts were improved, he measured lower values for resistivity, which have been confirmed by Hi-Z using the same metal contacting methods. The second independent verification was performed by Dr. Makoto Otani of NIST who essentially obtained the same results as Hi-Z and Prof. Bandaru. It is planned to perform further independent verifications of Hi-Z measured

can attain very high coefficients of performance (COP) to satisfy the requirements for cooling room temperature detectors. Multi-layer nanocomposite QW films (each 10 nm thick) were fabricated to demonstrate that Si/SiGe QW materials can be deposited on a low thermal conductivity substrate and provide at least the desired COP over the required temperature range of 250K to 350K in a single-stage nano cooler. These QW thermoelectric materials can also be implemented into commercial equipment in the air conditioning and refrigeration applications, thus eliminating fluids, ozone-impacting refrigerants and compressors. Thermoelectric properties, leading to these high COPs, have been independently verified by the researchers at UCSD and NIST. Even though conservative QW thermoelectric properties were used in the analysis, the predicted COPs satisfy the requirements with a large margin.

ACKNOWLEDGMENTS

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