DOE PHASE I FINAL REPORT

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**“Cost-Effective Fabrication Routes for the Production of Quantum Well Structures
and Recovery of Waste Heat from Heavy Duty Trucks”**

Budget Period 1

Submitted by:

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1. EXECUTIVE SUMMARY

The primary objectives of Phase I were: (a) carry out cost, performance and system level models, (b) quantify the cost benefits of cathodic arc and heterogeneous nanocomposites over sputtered material, (c) evaluate the expected power output of the proposed thermoelectric materials and predict the efficiency and power output of an integrated TE module, (d) define market acceptance criteria by engaging Caterpillar's truck OEMs, potential customers and dealers and identify high-level criteria for a waste heat thermoelectric generator (TEG), (e) identify potential TEG concepts, and (f) establish cost/kWatt targets as well as a breakdown of subsystem component cost targets for the commercially viable TEG. Phase I consisted of Tasks 1.1 – 1.6. Accomplishments made during Phase I included:

1. Engine conditions were defined for a Class-8 heavy-duty truck using data from a Caterpillar C15 engine. These data consisted of the engine speed and load, the exhaust temperatures, the thermal flux delivered to the thermoelectric devices, and the expected power out.
2. Application-specific conditions were defined for the thermoelectric devices. These consisted of the overall footprints, thicknesses, and geometries of the device, as well as the expected thermal flux through the device.
3. Application specific conditions were also defined for the thermoelectric materials, both P and N, as quantum well films and nanocomposites. These conditions included the expected ZT values based on projected seebeck (S), electrical resistivity (ρ) and thermal conductivity (κ) values, as well as expected specific power (Watt/g) and conversion efficiencies.
4. Various locations across an engine were evaluated for placement of the thermoelectric generator (TEG). Based on exhaust flow characteristics, projected power output, pressure drop requirements and conversion efficiencies, the best location was downselected.
5. A generic design for the TEG was developed in order to estimate volume requirements.
6. Several concepts for the cold size heat exchanger were developed. Based on size constraints, heat flow analysis, and pressure drop requirements, the best concept was downselected and a detailed design was generated.
7. Thermal analysis on the hot side of the TEG was completed, resulting in a best-in-class design for the heat and sink.
8. Truck modeling was completed on the downselected TEG configuration, giving an estimate for the overall fuel efficiency improvement.
9. Cost modeling was completed at the material and device level for three fabrication routes (sputtering, cathodic arc and heterogeneous nanocomposite). Two market cases and two heat flux conditions were evaluated. Process improvements were included over a commercialization timeline to reduce costs with time and a ProForma/Economic Analysis was completed to distinguish between cost to make and price to sell.
10. Cost modeling was completed at the system level using both a heat exchanger model and a discounted cash flow model to estimate the total price of the thermoelectric generator.
11. A marketing study was completed that determined the maximum acceptable cost/watt.
12. Acceptable cost/watt numbers were compared to the projected improvement on fuel efficiency and an overall assessment of feasibility/viability was made.
13. Risks at each level (material, device, system) were identified. Plans to mitigate each risk were also detailed.

A fuel economy improvement of 2.2% was determined that resulted in a market price of \$0.46/watt. The TEG selling price was determined to be \$0.51/watt. Based on these numbers, the generation of power using diesel exhaust was deemed economically viable. The More Electric Truck platform provided by Caterpillar is expected to give another 2 – 2.5% fuel economy improvement due to better utilization of electrical energy, resulting in a total fuel economy savings of 4 – 4.5%. The critical customer requirements for fuel economy savings were determined to be 2 – 9%. Therefore, based on the TEG design and the assumptions made in the cost modeling, the technology proposed was also deemed as also technically feasible

2. TECHNICAL PROGRESS

2.1. Task 1.1 – TE Material / Device Thermal and Performance Modeling

Performance modeling was carried out as the first step at both the material and device level in order to set boundary conditions for the thermoelectric generator (TEG). These boundary conditions depend upon the diesel exhaust temperature, mass flow, heat flux, and thermal resistances of the thermoelectric materials. From this, the thermoelectric module could be designed to optimum by matching the achievable heat flux from the gas stream to the optimum heat flux and temperature difference across the module. From CAT and Hi-Z/PNNL initial studies (to be discussed later in Section 2.2.3), it was determined that a module hot side temperature of 275°C and cold side of 100°C with a heat flux of 10 Watt/cm² through the thermoelectric device would optimize the power output. Later studies indicated that a heat flux of 25 Watt/cm² was possible and offered cost reduction opportunities. A module hot side temperature of 275°C and cold side temperature of 100°C with a heat flux of 25 Watt/cm² was used to determine the final thermoelectric generator design and system selling price.

From this high level analysis, the properties of both the quantum well (QW) films and heterogeneous nanocomposites were further refined. For the QW films, property data were based on both experimental and literature values [refs 3-11]. Because to date, the thermal conductivity of the Hi-Z sputtered films have not been determined directly and because the team wishes to be conservative in this regard, the bulk thermal conductivity values were assumed. ZT values ranging as high as 2.8 – 3.8 result when this thermal conductivity is combined with the measured Seebeck and Resistivity values (see Table 1), giving an average device ZT of 3.3. Also, because insufficient experimental data have been collected for the Si/SiC material system at Hi-Z, the assumption for the purpose of this study was that the resulting properties of the Si/SiC will be equivalent to that of the Si/Si_{0.8}Ge_{0.2} material system. If this assumption is not the case, unless the cost of the Si/SiC carbide system is significantly lower than the Si/Si_{0.8}Ge_{0.2} system, there will be no motivation to move to an “all carbide” system. This statement is true for both QW films and heterogeneous nanocomposite material. By making the properties of these two material systems equal, direct cost comparisons could be made. In all cases, these material properties will need to be verified during the first part of Phase II.

Table 1. Performance data projected for the QW films

Material System	N / P	Project Seebeck (μV/K)	Projected Resistivity (mohm-cm)	Projected Thermal Conductivity (Watt/m-K)	Mean Operating Temperature	Projected ZT	Projected Device ZT
Si/Si _{0.8} Ge _{0.2}	N	-1095	1.88	7.44	175 °C	3.8	3.3
B ₄ C/B ₉ C	P	1028	0.56	30	175 °C	2.8	

To illustrate the importance of choosing the right substrate for the QW multilayer films, Figure 1 gives the thermal conductivity values assigned to the films and compares these values to several candidate substrate materials. It is clear from these data that the substrates to be used for this application must have a thermal conductivity lower than the deposited film in order to reduce parasitic heat losses by thermal shunting and also to improve thermal efficiency through the film. Satisfying this requirement will be one focus in Phase II.

Figure 1. Assumed quantum well film thermal conductivity (bulk values) along with thermal conductivity values for some candidate substrates.

TE property values were also assigned to the heterogeneous nanocomposites. Because these materials have yet to be developed, the working assumption for the purpose of this study was that the resulting ZT values will be equal to that of the QW films. Based on literature data from Dresselhaus^[ref 1] and Huxtable^[ref 2], a thermal conductivity value of 1.8 Watt/m-K was assigned to the Si/Si_{0.8}Ge_{0.2} nanocomposite material, which is approximately 25% that of bulk. Similar to the reasons discussed previously, the same properties were assumed for the Si/SiC system. Assuming the same thermal conductivity reduction for the B₄C/B₉C nanocomposite materials, a value of 7.5 Watt/m-K was assigned. Normalizing these value to the projected ZT value of 3.3 for the QW films at a mean temperature of ~175°C, the following Seebeck (S) and Resistivity (r) values were determined. These will be regarded as target values for Phase II.

Table 2. Projected performance data for the QW nanocomposites

Material System	N / P	Projected Seebeck (μV/K)	Projected Resistivity (mohm-cm)	Projected Thermal Conductivity (Watt/m-K)	Mean Operating Temperature	Projected ZT	Projected Device ZT
Si/Si _{0.8} Ge _{0.2}	N	-533	2.15	1.8	175 °C	3.35	3.30
B ₄ C/B ₉ C	P	533	0.54	7.5	175 °C	3.25	

Specific power (Watt/g) values were then determined for the QW films and heterogeneous nanocomposites. These values relate directly to the thermal conductivity values assigned above.

They were determined to be 1.0 Watt/g for the QW films and 3.15 Watt/g for the nanocomposite material.

To demonstrate the strong impact of thermal conductivity on specific power, a parametric study was carried out in which the figure of merit value, ZT , was held constant, but the thermal conductivity value that makes up that ZT was changed. From this, it was found that the material's thermal conductivity, κ , has a greater impact on specific power than does Seebeck coefficient, α , or electrical resistivity, ρ . This result is important, since the specific power has a direct impact on the amount of material required and therefore the cost. As can be seen in Figure 2, a reduction in thermal conductivity from 6 to 3 Watt/m K increases the specific power by a factor of two.

Figure 2. Specific power improvements as a function of lower thermal conductivity

2.2. Task 1.2 – Waste Heat Generator Concept Development

2.2.1. TEG Requirements Definition

The team's approach to defining concepts around a thermoelectric generator (TEG) and eventually achieving an optimum design was iterative. For the Phase I effort, a set of high-level requirements for the envisioned TEG system was first defined. These requirements take into consideration (i) design features of the TEG and (ii) value to the customer. Table 3 provides a list of the nine most critical customer requirements (CCR) and their corresponding rank based on the weighted score

Table 3. Thermoelectric generator (TEG) system level requirements

No.	CCR	CCR Rank
1	Fuel Savings	100
2	Emission Measures	94
3	ΔT Across TE module	91
4	Purchase Price	77
5	Durability	76
6	Pressure Drop	69
7	Reliability	50
8	Number of OEM components needing redesign/retrofit	55
9	Generator Volume	52

The amount of fuel savings provided by the TEG was found to be the most important critical requirement that drives customer value.

2.2.2. Exhaust Flow Characteristics

For the concept generation and downselection process, several key design parameters were identified, the first of which was the exhaust flow characteristics. Since the target application for the TEG is an on-highway heavy-duty truck, engine data for a Caterpillar C15 engine (rated at a peak power of 317kWatt) was collected. Although engine simulation is one potential source of data, the team decided to use actual test cell data generated from the specific engine being targeted, which is currently installed on a Caterpillar MorElectric Truck. The data were collected for three different engine speeds and at four different engine loads. Since the envisioned TEG will be operating most of the time under nominal truck cruising conditions, an exhaust temperature of 353°C and flow rate of 0.36 kg/s were chosen as set design parameters, corresponding to the conditions at an engine load of 50% and speed of 1500 rpm.

2.2.3. TEG Sizing, Location and Generic Design

Installation of the TEG was focused initially on two possible locations: (i) within the engine compartment and (ii) under the truck chassis. To determine the best location of the TEG, a preliminary size for the TEG was estimated and compared to the allowable size requirements identified in Table 3. A numerical model was then developed using a heat flux based analysis. Model inputs included (i) physical properties of the thermoelectric materials, (ii) desired cold side temperature, and (iii) desired electrical power output

From this data, the area and thickness requirements for the thermoelectric material were identified for three different heat fluxes, 10 Watt/cm², 25 Watt/cm² and 50 Watt/cm², assuming a target electrical output of 5kWatt, a temperature differential of 175°C, and a thermoelectric material Z value of 7.34 E-03 K⁻¹. Using a module footprint of 39.31 cm², typical for a Hi-Z 40 Watt module, the total number of modules required was then calculated. A generic design for the generator was then built around these numbers of required modules, for the three above-mentioned cases noting that the modules would be distributed evenly across the two planes that make up the exhaust flow direction.

The generic design includes the estimated volume requirements for an array of finned heat sinks on both the hot side and cold sides of the modules, where the sinks have a total length and width comparable to that of the thermoelectric modules. Figure 3 shows a schematic for the generic TEG at a heat flux of 25 Watt/cm², while Table 4 gives the size estimates for such a generic TEG at the three heat fluxes chosen.

Figure 3. Schematic of a generic TEG at a TE material heat flux of 25 Watt/cm

Table 4. Size estimates for the TEG at three different heat fluxes.

Heat Flux (W/cm ²)	Power Output (kW)	T _{cold} (°C)	T _{hot} (°C)	Delta T	Thermal Power Into TE Devices (kW)	Conversion Efficiency	Thermal Power Out of TE Devices	TE Material Area Required (cm ²)	Number Of TE Modules	Power Per Module (Watts)	TEG Width (m)	TEG Length (m)	TEG Height (m)
10	5	100	275	175	39.7	12.58%	34.7	3975	100	50	0.7	0.7	0.45
25	5	100	275	175	39.7	12.58%	34.7	1590	40	125	0.4	0.4	0.45
50	5	100	275	175	39.7	12.58%	34.7	795	20	250	0.28	0.28	0.45

Table 4 also shows additional outputs that were used for preliminary hot side thermal analysis. For a fixed electrical power output of 5kWatt, the thermal power that needs to be delivered to the TE modules was equal to 40 kWatt at a TE device efficiency of 12.58%. Worth noting is that this thermal power can be reduced if the ZT of the TE material is increased and/or if the TE device temperature difference becomes larger than the 175°C value chosen for the analysis. Based on the relative sizes of the TEG at the three different heat fluxes, the conclusion from this analysis was that the TEG could not be placed anywhere within the engine compartment unless the design heat flux was greater than 50 Watt/cm². The best location identified for the envisioned TEG is therefore under the truck chassis. The TEG size requirements at a thermoelectric heat flux of 25 Watt/cm² through the TE device appeared to be reasonable and were therefore used for the further analysis.

Several thermal design iterations were performed to determine the expected device hot side temperature at each heat flux. It was found that a 100°C temperature gradient in the exhaust flow is required to extract 40 kWatt of energy from the specified exhaust mass flow rate. This temperature gradient results in an exhaust exit temperature of 253°C. If the single stage heat exchanger shown in Figure 4 is used, the average base temperature where the thermoelectric device would be arranged could not be hotter than the exit exhaust temperature. This key point led to an analysis of a 10-stage counter flow heat exchanger. This design divides the TEG into 10 sections, each with an array of fins on the hot side to extract energy from the exhaust and deliver it to the TE devices and another array of fins on the cold side to dissipate the unconverted energy.

2.2.4. TEG Concept Generation

Using the heat flux based model described above, thermal specifications were identified for the TEG and concept generation was initiated. For a fixed electrical power output of 5kWatt and a device efficiency of 12.6%, 40 kWatt of thermal energy needs to be extracted from the exhaust. This relatively large amount of thermal energy requires a pair of high performance heat exchangers that have low thermal resistance and are compact enough to fit within the maximum allowable volume. Expanding on the generic TEG design shown in Figure 3, four system level concepts were identified that showed promise for delivering such high thermal performance. All concepts accomplished energy extraction from the exhaust through an array of finned surfaces (see Section 2.2.5 for more details). On the cold side, a similar but not exact arrangement of fins would also be used. Because of the very high temperature exhaust, even at nominal cruising conditions, aluminum and copper were ruled out as potential fin materials on the hot side,

although they could be used on the cold side. The major distinction between the four concepts is the choice of fluid and method of fluid delivery on the cold side.

2.2.5. TEG System Analysis and Downselection

Thermal analysis of the TEG was focused on (i) designing the hot side heat exchanger for maximum heat delivery into the thermoelectric devices, (ii) analyzing, in detail, the four system level concepts described above for the cold side heat exchanger (extraction of heat out of the thermoelectric devices), and (iii) downselection of an appropriate thermal management configuration which would likely involve the use of heat pipes. This work was outsourced as a task to a company called Advanced Cooling Technologies (ACT)

As a first step, ACT identified an optimal fin design for the hot side heat exchanger. The large exhaust temperature drop of 100°C was the predominant driver in the overall hot side heat exchanger design. Several fin pitches and thicknesses were analyzed. A large fin pitch is desirable due to its ability to lower the thermal resistances and therefore heat losses across the fin during delivery. However, the magnitude of pitch is realistically limited by manufacturing. The largest fin pitch able to be manufactured was therefore chosen as optimal. The size of the each heat sink on the hot side was then optimized such that the overall TEG pressure drop remains within allowable limits.

For the cold side heat exchanger, ACT analyzed in detail the four concepts generated. Preliminary analysis demonstrated that the *Forced Coolant Cooling (FCC)* concept generated higher electric power than the other air-cooling concepts. The air-cooling concepts were found to be challenging from a design perspective, since the air has to be delivered in a counter flow manner with respect to the exhaust gas. This counter flow design requires the exhaust flow to be redirected 180° upstream of the TEG and then redirected back 90 -180° downstream of the TEG. These redirections add significant backpressure on the engine, thus reducing the overall value of the TEG.

Liquid cooling, on the other hand, can be easily delivered to the TEG in a counter flow manner using appropriate hoses and preexisting engine ports with coolant out options. Liquid cooling also offers the advantage of smaller volume and weight. The reduced volume and weight is beneficial from a cost point of view and a fuel consumption penalty. The *Forced Coolant Cooling (FCC)* concept was therefore downselected as the best design for the cold side of the TEG.

Although the size of the TEG was acceptable, the estimated weight of the TEG was close to 772 kg. This large weight and associated cost were major design disadvantages. The root cause for the large volume and weight was linked to the hot side heat sink. The maximum allowable exhaust pressure drop and the exhaust temperature design point of 353 °C determined the hot side heat sink size.

Since the team was restricted to the maximum allowable pressure drop, a sensitivity analysis was conducted to understand the impact of a higher exhaust temperature on the TEG size and weight. Keeping the desired electrical power of TEG the same, and assuming a 50°C higher exhaust temperature, the sink geometry on the heat delivery side was recalculated. In this case, the higher exhaust temperature allows for a more thermally resistant sink. Typical heat sink thermal resistance to volume relationships show that a 50% increase in thermal resistance results in a

400% reduction in sink volume. The new sink size calculated for the higher exhaust temperature shows that the size of the TEG could be reduced by a factor of 10 and the weight of the TEG was reduced by a factor of 7.

There are several test data sets, other than the conservative set used by the team initially, that suggest a higher exhaust temperature of 403 °C is possible at truck cruising conditions. Therefore, the team decided to use the modified heat extraction sink size for further cost and truck modeling activities. The overall TEG dimensions are shown in Figure 4.

Figure 4. Layout and dimensions of the down selected thermoelectric generator

Although extensive thermal analysis was conducted to reach this design, it is still very sub-optimal, several shortcomings exist and more analysis is required. The weight and size of the TEG need to be reduced to increase the power to weight ratio. The main driver for large weight and size is the large number of fins required for the hot side heat sink. The opportunity exists to explore other fin geometries that increase the overall heat transfer coefficient on the hot side. This higher heat transfer coefficient would reduce the TEG size. The fin material, which in this first generation design is iron based, (stainless steel, carbon steel or graphitic cast iron) is very dense and contributes significantly to the overall weight. Other lighter; low cost material alternatives such as metallic foams could be researched further for its applicability to the hot side heat sink. During Phase III, the team will conduct additional analysis to reach a final design concept based on updated data and believes that a significantly improved TEG design can be identified.

2.3. Task 1.3 – Waste Heat Generator System Analysis (Truck Modeling)

Activity under this task was focused on developing and enhancing numerical models that allowed the evaluation of the impact of the TEG on the fuel consumption and overall truck engine efficiency.

Prior to this contract, an integrated TEG-heat exchanger design model was developed at Caterpillar. Given the hot side fluid conditions, the thermoelectric material properties, and the thickness of the thermoelectric devices, the model estimates the number of couples, area of thermoelectric devices, electric power output, efficiency, and the cold side fluid conditions as a function of operating hot side and cold side temperatures. The main use of the design model is to optimize the area of the thermoelectric devices, thereby maximizing electrical power output. As part of this contract effort, this model has been enhanced to conduct performance calculations. In this case, the module size is fixed and the model predicts the actual hot side temperature, cold side temperature, electrical power output, and conversion efficiency for a given set of hot side and cold side fluid conditions.

In parallel to this contract effort, a complete-system model was developed of a Caterpillar MorElectric Truck (MET) using Simulink and Dynasty (Caterpillar's proprietary dynamic

simulation code). The model included the engine, power train, truck mass, cooling system, electrical system and thermoelectric generator. For a given set of road conditions and desired truck velocity, the model determines the forces acting on the truck and the performance (temperatures, fuel rate, heat loads, speeds, voltages, etc) of the engine, cooling, and electrical systems. Exhaust flow and temperature are fed to the TEG portion of the model and the resulting electrical power and coolant heat load are in turn fed to the electrical and cooling systems. The TEG electrical power is routed through a DC/DC converter to the Integrated Starter Generator (ISG) circuit, first to run the electrical accessories and second to provide motoring capability to assist in the propulsion of the truck.

The truck model simulated the performance of the MET with and without a TEG at three separate grades. The truck was fully loaded and traveling at 107 kph (66.5 mph) on a constant-slope road for 100 km at a 15.4 °C ambient temperature. The exhaust gas properties were assumed similar to those of air, and the exhaust gas was directed through the TEG. The thermoelectric material properties were considered constant. The heat transfer coefficients for the TEG heat exchangers were supplied by ACT. The DC/DC converter was assumed 90% efficient. The results for engine power, TEG power, and fuel savings compared with the baseline (no TEG) truck are shown in Table 5. Increasing grade produces greater engine load, which in turn produces more TEG electrical power. However, the increased heat load to the cooling system from the exhaust through the TEG causes the radiator's cooling fan to operate at a higher speed. The increased electric power to the fan reduces the benefit of the TEG on fuel savings. The added weight of the TEG also affects the fuel savings as indicated by the difference in fuel savings for the TEG design having no additional weight and the TEG design weighing 105 kg.

Table 5. Truck-TEG Model Simulation Results

	0° (0%) Grade			0.2° (0.35%) Grade			1.14° (2%) Grade		
	Base-line MET	MET with 0 kg TEG	MET with 105 kg TEG	Base-line MET	MET with 0 kg TEG	MET with 105 kg TEG	Base-line MET	MET with 0 kg TEG	MET with 105 kg TEG
Engine Power (kW)	148.4	144.9	145.1	184.1	179.7	180.0	348.7	341.2	342.4
TEG Power (kW)	0	4.33	4.34	0	5.54	5.55	0	11.8	11.8
Fuel Savings (%)	---	2.4	2.1	---	2.4	2.2	---	1.9	1.6

The results given in Table 4 indicate that a 2.2% fuel savings is achievable for the current MET/TEG configuration under cruising conditions. A fuel savings of up to two and a half percent has also been demonstrated for the MET compared with a Class 8 truck without the MorElectric features. Thus, a total fuel savings of 4 – 4.5% is possible for a MorElectric truck with a thermoelectric generator compared with a conventional Class 8 truck with an alternator. In addition, to further improve the fuel savings, the team plans to investigate power management controls to optimize the cooling fan and ISG interactions with the TEG and to study ways to use ram air to help cool the heat from the cold-side exchanger before it is dumped to the radiator circuit.

2.4. Task 1.4 - Cost Modeling

2.4.1. Material Cost Modeling

To estimate the relative costs of the TE materials, three cost models were generated representing the proposed three fabrication routes– one for sputtering (at Hi-Z/ PNNL), one for cathodic arc

deposition (at UTRC/PW) and one for synthesis as a heterogeneous nanocomposites (at UTRC). Each model was unique in that it took into consideration the particular aspects of each material process but at the same time the cost models were made self-consistent by making common input assumptions (e.g., market, market penetration, volume discounts applied to raw materials, substrate and substrate costs, cathode and target costs, commercialization timeline, and labor charges). The output data are therefore directly comparable for the different fabrication routes. The models were developed primarily to generate cost/g and cost/W values, but have also been used to (i) generate costs across a timeline to commercialization and (ii) define process changes as a function of time to ensure acceptable cost

2.4.1.1. Sputtering Fabrication Route Cost Modeling

The cost model built for the sputtering fabrication route was done at Hi-Z/PNNL for six production levels ranging from 20 to 100,000 kg per year. The cost model includes estimated materials, labor, overhead, G & A, profit, and contingency to arrive at estimated selling prices for each level of production in dollars per watt and dollars per kilogram. In addition, a stepwise program to improve yields and throughput of the sputtering fabrication process, to lower costs, and to reduce the selling price was determined over a six-year period. This program involved such steps as moving to less expensive targets and substrates and automation of equipment. The material selling price was found to be substantially reduced by using this stepwise, long-term process improvement program, see Table 6. These selling prices were generated for a 10 Watt/cm² heat flux. The process improvements, in conjunction with increased production levels, would occur together as a function of time for the overall packaged device.

Table 6. Material Selling Prices for the Sputtering Fabrication Route (10 Watt/cm² heat flux)

Market Penetration	Year 1 \$/watt	Year 2 \$/watt	Year 3 \$/watt	Year 4 \$/watt	Year 5 \$/watt	Year 6 \$/watt
Si / Si_{0.8}Ge_{0.2} – B₄C / B₉C						
34%	2.35	1.65	1.53	0.50	0.40	0.34
100%	1.56	1.09	0.78	0.33	0.27	0.24

A full graphical cost comparison at the material level between fabrication routes can be found in Section 2.4.1.3. Key observations made from the sputtering cost modeling effort were:

Key observations (Sputtering):

- The average estimated selling price for the sputtered material was found to range from \$1.92 per watt in the first year to \$0.29 per watt in the 6th year. For comparison, current Hi-Z commercial modules are ~\$5/Watt and so the initial process improvements shown here are expected to provide a competitively priced product.
- Capital costs were found to be less of a driver for the sputtering fabrication route than for cathodic arc fabrication route (section 2.4.1.2.3), particularly in the first year.
- The major cost drivers for the sputtering fabrication route were the target costs, the substrate costs, and the raw material costs.
- Key risks associated with the sputtering fabrication route are the large area needed for the equipment, the assumption that this equipment can be built, and the assumption that homogenous material can be fabricated over the large area.

- Year 2 process change gives a 30% cost reduction over Year 1. Year 3 process change gives a 7% cost reduction over Year 2. Year 4 process change gives a 67% cost reduction over Year 3. Year 5 process change gives a 20% cost reduction over Year 4. Year 6 (automation) gave a 15% cost reduction over Year 5.

2.4.1.2. Cathodic Arc / Heterogeneous Nanocomposite Cost Modeling

2.4.1.2.1. Process

The cost model was divided into two sections: the process model, which was used to determine the annual operating cost of the plant and the specific cost of the product, and the economic analysis, which was used to determine the selling price, value to the investor (NPV), and process improvements needed to balance production costs with cash flow requirements. Two production scales were assumed - that representing the current diesel market captured by Caterpillar (34%) and that representing the entire diesel market. The cost models were used to: (a) downselect synthesis processes that give the greatest potential value to the customer and the investor for the heterogeneous nanocomposite route and (b, define process improvements as a function of time to reduce costs for the cathodic arc deposition route.

The first step in the cost modeling process was the definition of expected market penetrations. These values were used to determine the total kg production targets for each market penetration case and the kg production quantities per year for each fabrication route. For cathodic arc route, the material systems were modeled together as a P-N couple. For the nanocomposite route, because of its added level of complexity (e.g., multiple synthetic routes for each material system requiring different chemicals and equipment), the P and N leg were modeled separately and then combined to make the couple. The raw material requirements for each year were then calculated using mass and energy balances. The processing steps, time requirements, and utility consumption rates were then determined. The number of batches and the processing time per batch for deposition were specified to determine the annual operating hours and number of machines required in each plant. Once the processing steps were defined, the plant labor requirements were analyzed and the capital costs of the required equipment were entered for each section of the plant. From this, the annual operating cost per unit of product was calculated.

2.4.1.2.2. Economic Analysis

In order to downselect to the most promising concept for each process, a more detailed look at the plant cash flow profile and NPV was required. Based on the capital costs, annual production rates, estimated operating costs, and plant life, the financial plan for the facility was analyzed. A hurdle rate (or discount factor) was entered, which accounts for the time value of money, the inflation rate, and the maintenance cost factors. Based on this hurdle rate, the annual average production price to the customer was calculated. Once the parameters for the economic analysis were appropriately adjusted for each process, the product selling prices were compared to downselect the most cost-effective routes to pursue for further technology development.

2.4.1.2.3. Cathodic Arc Results

Similar to that done for the sputtering fabrication route, process improvements were defined for the cathodic arc fabrication route over a 6-year period. The selling price was found to be substantially reduced with this stepwise long-term process improvement program, see Table 7. These selling prices were generated for a 10 Watt/cm² heat flux.

Table 7. Cost Modeling Results for the Cathodic Arc Fabrication Route (10 Watt/cm² heat flux)

Market Penetration	Year 1 \$/watt	Year 2 \$/watt	Year 3 \$/watt	Year 4 \$/watt	Year 5 \$/watt	Year 6 \$/watt
Si / Si_{0.8}Ge_{0.2} – B₄C / B₉C						
34%	7.28	1.96	1.21	0.70	0.57	0.47
100%	4.54	1.09	0.80	0.48	0.40	0.34
Si / SiC – B₄C / B₉C						
34%	10.07	2.35	1.37	0.69	0.54	0.43
100%	7.18	1.30	0.91	0.47	0.37	0.31

As with the sputtering fabrication route, these process improvements would occur in conjunction with increased production levels as a function of time and also with process improvements at the device level. A full graphical cost comparison at the material level between fabrication routes can be found in Section 2.4.1.3. Key observations made from the cathodic arc cost modeling effort were:

Key observations (Cathodic Arc):

- The average estimated selling prices for cathodic arc material was found to range from \$7.26 per watt in the first year to \$0.39 per watt in the 6th year
- Capital cost was determined as the critical driving factor due to the very large markup value required to achieve plant profitability.
- Raw material costs were found to be the primary operating cost, making up more than 96% of the annual operating cost estimate. In order to meet the target material price requirements, the cathode costs must be reduced by up to 80 – 95% from current laboratory chemical catalog costs.
- Electricity, at 3% of the annual operating cost, is not a significant cost driver.
- Labor costs, at less than 1% of annual operating costs, are not a significant cost driver
- Year 2 gave a 77 % cost reduction over Year 1. Year 3 gave a 34 % cost reduction over Year 2. Year 4 gave a 45 % cost reduction over Year 3. Year 5 gave an 18 % cost reduction over Year 4. Year 6 gave a 17 % cost reduction over Year 5.

2.3.1.2.4. Heterogeneous Nanocomposite Results

For the heterogeneous nanocomposite fabrication route, fifteen different synthetic routes were analyzed. These routes were selected from a larger set of routes as being the most cost effective. They should be considered as a general class or category for synthesis. When inspected in detail, each synthetic route can be broken down into many different pathways for synthesis, depending on the exact process details. Phase II activities will entail defining and developing the downselected processes through a materials development effort to maximize the performance of the material. With each process refinement step made in the laboratory, the cost models will be updated and the fabrication costs refined.

Delivered to the *device* cost model (see Section 2.4.2) was the average cost per watt for each material system. This value is believed to be the most conservative and also the most probable. Unlike sputtering or cathodic arc fabrication routes, process improvements were not built into the

model over the 6-year period. It is assumed that the lowest cost route will be determined at the start of the 6 years and cost reduction thereafter will be driven by discount factors applied to chemicals due to large volume production, see Table 8. These selling prices were generated for a 10 Watt/cm² heat flux.

Table 8. Cost Modeling Results for the Heterogeneous Nanocomposite Fabrication Route (10 Watt/cm² heat flux)

Market Penetration	Year 1 \$/watt	Year 2 \$/watt	Year 3 \$/watt	Year 4 \$/watt	Year 5 \$/watt	Year 6 \$/watt
34%	2.54	1.18	0.84	0.74	0.64	0.52
100%	1.90	0.79	0.60	0.57	0.50	0.42

A full graphical cost comparison at the material level between fabrication routes can be found in Section 2.4.1.3. Key observations made from the heterogeneous nanocomposite cost modeling effort were:

Key observations (Heterogeneous Nanocomposite):

- The average estimated selling prices for the nanocomposite materials range from \$2.22 per watt in the first year to \$0.49 per watt in the 6th year.
- The largest cost driver for the nanocomposite route was the chemical precursor material.
- The second cost driver for the nanocomposite route was the capital costs.
- Capital costs for the nanocomposite materials were significantly lower than for the deposition routes (\$2-23M versus \$48-96M).
- Capital costs increased linearly with production costs since equipment is bought only when needed and costs reductions were not applied to capital equipment with time.
- There were not significant cost savings in the 100% market case over the 34% market case, due to the fact that the largest chemical discounts were seen in the early years and larger production scales did not offer larger chemical discounts.
- Labor, solvent, and processing costs were the least significant driver of cost.
- Cost reductions were largest in the early years due to discount factors on chemicals in going from specialty to production scale quantities. (54% reduction in Year 2 compared to Year 1 and 26% reduction in Year 3 compared to Year 2)
- Cost reductions tailed off in the 4th year (8% reduction in Year 4 compared to Year 3)
- Cost reductions picked back up in the 5th and 6th year (50 and 17% reduction, respectively) due to capital equipment depreciation.

2.4.1.3 Material Selling Price Comparison

Figure 5 shows the overall selling price comparison for the three fabrication routes for the two market cases studied. Over the 6-year period, a 3-year payback is observed for the three fabrication routes. The cathodic arc fabrication route shows higher selling prices in the first year due to the assumption that a facility will be built from the start while the sputtering fabrication route assumes the use of an existing sputtering facility. The selling prices are quickly reduced,

however, in the out years and were found to be lower than the sputtering fabrication route in the third year. At the end of the 6 years, the material selling prices are roughly equivalent. It will not be until Phase II that the team can assess, based on gathered experimental data, performance benefits offered by the cathodic arc fabrication route.

The heterogeneous nanocomposite route was found to be the most cost-effective process for the first three years, after which the deposition routes become more favorable due to automation of equipment. Considering the large number of assumptions built into each cost model, the overall conclusion is that all three fabrication routes offer the potential for commercialization, assuming continuous process changes and increased volume demand. Also, all three fabrication processes can be made profitable and give a payback in three years.

Figure 5. TE Material Costs (\$/watt) for each of the three fabrication routes for 34 and 100% Market penetration.

2.4.1.4. Selling Price Reduction Due to Higher Heat Flux

Additional system analysis by Caterpillar indicated that a heat flux to the device surface of 25 Watt/cm² was possible. This larger heat flux translates to a larger specific power (Watt/g) for each thermoelectric material (see Figure 6 below) and therefore a cost reduction at the material level.

Figure 6. Effect of Increased Heat Flux (W/cm^2) on Specific Power (W/g)

This difference in specific power was found to be significant. The previously discussed cost modeling was carried out for a heat flux of $10\text{ Watt}/\text{cm}^2$. Table 9 summarizes the effect on specific power (Watt/g) of increasing the heat flux to $25\text{ Watt}/\text{cm}^2$.

Table 9. Specific Power (W/g) of each Material as a function of Thermal Flux (W/cm^2)

Material	Material Form	Specific Power at $10\text{ W}/\text{cm}^2$	New Specific Power at $25\text{ W}/\text{cm}^2$
Si/Si _{0.8} Ge _{0.2} or Si/SiC	Film	1.50 W/g	6.40 W/g
B ₄ C/B ₉ C	Film	0.48 W/g	1.85 W/g
Si/Si _{0.8} Ge _{0.2} or Si/SiC	Nanocomposite	4.80 W/g	22.6 W/g
B ₄ C/B ₉ C	Nanocomposite	1.50 W/g	6.35 W/g

A 4 to 5-fold increase in specific power resulted, meaning that now only $1/4^{\text{th}}$ to $1/5^{\text{th}}$ of the original material is required to produce the same power. Less capital equipment is therefore required and also less chemical materials. The impact on overall material selling price is shown in Table 10. These reduced material selling prices were used by Hi-Z to determine the TE device selling price.

Table 10. Material Selling Price Reduction Due to the Higher Heat Flux

	Year 1 \$/watt	Year 2 \$/watt	Year 3 \$/watt	Year 4 \$/watt	Year 5 \$/watt	Year 6 \$/watt
Sputtering (\$/watt)						
10 W/cm ²	\$1.49	\$1.17	\$0.90	\$0.33	\$0.27	\$0.23
25 W/cm ²	\$1.34	\$0.88	\$0.59	\$0.15	\$0.11	\$0.09
Cost Reduction (%)	10%	25%	34%	55%	59%	61%
Cathodic Arc Deposition (\$/watt)						
34%	\$5.86	\$1.20	\$0.86	\$0.48	\$0.39	\$0.33
100%	\$2.22	\$0.46	\$0.33	\$0.19	\$0.15	\$0.13
Cost Reduction (%)	62%	62%	62%	60%	62%	61%
Heterogeneous Nanocomposite (\$/watt)						
34%	\$1.93	\$0.85	\$0.66	\$0.62	\$0.54	\$0.46
100%	\$0.60	\$0.26	\$0.18	\$0.16	\$0.15	\$0.12
Cost Reduction (%)	69%	68%	70%	72%	72%	72%

Note: Cost comparisons were made only for the 100% market case and were averaged across the two possible couple configurations (Si/SiGe – B₄C/B₉C and Si/SiC – B₄C/B₉C).

2.4.2. TE Device (without material) Cost Modeling

For the purpose of designing and costing the TE devices that will house the various quantum well structures, the module footprint was set on the same scale as Hi-Z's commercially available HZ-14 Bi₂Te₃ module. Available for this study was substantial information from Hi-Z on both the performance and cost of this commercial module over the past several years. For the quantum well module, cost-versus-performance benefit trade-offs were established to determine the exact sizing. These tradeoffs include such details as the depth, the type of quantum well material (nanocomposite, film), film thickness and substrate material (if applicable), and thermoelectric element length/area ratio. If packaged as quantum well films, the available area must include both the films and substrates. If fabricated as a heterogeneous nanocomposites, the area will be filled with single n and p-elements. Since the thermal resistance of quantum well thermoelectric materials is expected to be significantly different than the HZ-14 Bi₂Te₃ module, the depth of the module, substrate material, film thickness and various material thermal conductivities have been selected to optimize the performance vs. cost for this heavy duty diesel truck application. The results of the TE device cost modeling effort are given in Table 11 and Figure 7.

Table 11. Cost Modeling Results for the TE Device without TE material

Market Penetration (%)	Material System	Year 1 \$/watt	Year 2 \$/watt	Year 3 \$/watt	Year 4 \$/watt	Year 5 \$/watt	Year 6 \$/watt
Sputtering							
34	Si/Si _{0.8} Ge _{0.2} – B ₄ C/B ₉ C	6.22	4.12	2.38	1.38	0.66	0.17
100		4.02	2.35	1.38	0.73	0.16	0.04
Cathodic Arc							
34	Si/Si _{0.8} Ge _{0.2} – B ₄ C/B ₉ C	6.22	4.12	2.38	1.38	0.66	0.17
100		4.02	2.35	1.38	0.73	0.16	0.04
Nanocomposite							
34	Si/Si _{0.8} Ge _{0.2} – B ₄ C/B ₉ C	4.35	2.88	1.67	0.96	0.46	0.12
100		3.52	1.46	0.74	0.46	0.16	0.04

Figure 7. Comparison of the packaging costs (empty device) for each fabrication route.

Key observations (TE Device):

- The projected selling prices for a quantum well module (empty) at the same footprint as HZ-14 was found to range from \$4.39 per watt in the first year (on average) to \$0.10 per watt in the 6th year.
- For the multilayer films, the first two process step changes render the quantum well module competitive with today's HZ-14 commercial module in terms of selling price per Watt. The cost reduction in Year 2 is 40% lower than in Year 1.
- Year 3 process improvement reduces the selling price of the empty module by another 43%.
- The cost of packaging the nanocomposite materials is significantly less than the multilayer films due to a smaller number of process steps and an overall smaller device geometry.
- Cost reduction in Year 4 compared to Year 3 is another 43%. Cost reduction in Year 5 compared to Year 4 is very large at 63%. Cost reduction in Year 6 compared to Year 5 is the largest at 75%

Methods were also determined to reduce the quantity of material in each module and consequently the cost of fabrication at the device level. These methods have pointed to several potential approaches for Phase II development. One approach is to funnel or focus the heat flux through the quantum well material by diverting heat from the packaging material into and through the thermoelectric material. By using a device surface heat flux of 10 Watt/cm² and retaining the same thermoelectric power, a heat flux concentration of 2.5 reduces the required amount of quantum well material by over a factor of 5, see Figure 8 below.

Figure 8. Effect of Funneled heat flux on amount of TE material needed.

2.4.3. TEG System Cost Modeling

Initial selling price targets were established using a fuel savings benefit approach. This approach relies on the available data for the average miles driven per year for long haul heavy-duty applications, the annual fuel consumption per truck and the projected fuel savings discussed in the previous section.

2.4.3.1 Marketing Study

Figure 9 shows the results of a marketing study conducted by Caterpillar, which shows an average of 125,000 miles driven by truck owners (and operators) on an annual basis. Assuming an average fuel rate of 6 miles per gallon for heavy-duty trucks at a cost of \$2.4 per gallon, the annual average fuel consumption per truck is 21,833 gallons/truck/year with a cost of \$52,400/truck/year. Since the truck model showed that the TEG could potentially save 2.2% in fuel usage, a potential fuel savings of \$1153 per truck per year is projected. For an average truck life of 48 months, the total benefit would be in the range of \$4612. A selling price target for the TEG would be \$2306 assuming an average payback time of 24 month. For a 5kW generator, a \$/watt selling price target would then be \$0.46/watt.

Figure 9. Data collected from a marketing study conducted by Caterpillar in response to the question "How many miles have you driven over the last 12 months?" given to a multitude of truck owner and operators

The market case for selling TEGs was also investigated for an early adopter, such as the US Army. In this case, the cost of fuel was estimated as being several multiples of the cost of fuel for civilian applications. In several discussions between Caterpillar representatives and Army program managers, a conservative cost per gallon for diesel fuel for military applications was \$40 per gallon during combat situations. The average Army vehicle travels 144,000 miles per year. Assuming a fuel rate of 6 miles per gallon, the annual average fuel consumption per Army vehicle would then be 24,000 gallons with a cost of \$960,000 per vehicle per year. Since the expected TEG fuel savings is 2.2%, a potential fuel savings of \$21,120 per vehicle per year is projected. If a similar average life per vehicle was set at 48 months, the total benefit would be \$84,480. A selling price target for the TEG would be \$42,240 assuming an average payback time of 24 months. For a 5kWatt TEG, a \$/watt selling price target would then be \$8.45/watt.

2.4.3.2. TEG System Cost Modeling Results

Once the final TEG concept was downselected, cost models were created to estimate the overall manufacturing costs as well as the selling price of the TEG system. The TEG system consists of a heat delivery subsystem, a heat extraction subsystem, thermoelectric modules, a DC-DC power converter, and casing. As a first step, the costs for each subcomponent were established. For the heat delivery and extraction subsystems an independent cost model was created. A discounted cash flow model (DCF) was then created. This model considered not only the costs of the TEG system, but also costs associated with building an assembly plant.

2.4.3.2.1 Heat Exchanger Cost Modeling

The heat exchanger consists of a heat delivery subsystem, a heat extraction subsystem, thermal insulation, and casing. Results from the heat exchanger cost modeling are shown in Table 12. An analysis of the results reveals that the cost for the heat delivery subsystem was the main contributor to the overall cost of the heat exchanger.

Table 12. Heat exchanger cost modeling results

Coolant- Engine		Units
Heat Delivery Cost Per Generator	\$ 718.66	\$
Heat Extraction Cost Per Generator	\$ 53.13	\$
Casing Cost Per Generator	\$ 90.70	\$
Total Cost Of Heat Exchanger Per Generator	\$ 862.50	\$
Generator output	5000	watt
Cost Per Watt	\$ 0.17	\$/watt

2.4.3.2.2 Power Electronics Costs

To maintain a constant voltage supply from the thermoelectric devices to the main MorElectric truck bus, a DC-to-DC converter was a necessary component that had to be accounted for in the overall TEG design and cost. The power specification for converter was set at 5 kW. The team investigated the cost of several off the shelf or near production converters/inverters that had similar characteristics to the envisioned converter and arrived at an initial cost estimate for the DC-to-DC converter of \$0.3/watt using current technology, with a 20% discount on a yearly basis for near future cost effective technology enhancements and volume discounts.

2.4.3.2.2 Discounted Cash Flow Modeling

The discounted cash flow model was created to estimate the selling price for the TEG system once all costs of components were rolled up, including the cost of the thermoelectric devices as provided by Hi-Z Technology. In addition to the component costs, the discounted cash flow model included the cost of labor, capital depreciation and overhead for running an assembly facility. The minimum selling price was determined such that the total investment could be recovered over a 6-year market penetration period.

The calculation of the selling price assumed two market segments existed. One segment was the on-highway heavy-duty truck market while the other was early adopter market. For the on-highway truck market, the total market size was estimated used to be 220,000 trucks per year. The total Caterpillar market for the TEG systems was modeled after the current market share that Caterpillar attains on average for heavy-duty engines, which is estimated to be 27% of the total market. Therefore, the market size was set at 61,000 TEG units by year 6.

On the other hand, for the early adopter market, such as the Army vehicles market, Caterpillar's current engine sales to the Army averages around 2000 units per year. The team assumed that market would grow from 1,100 TEG systems in year 1 to 5000 systems by year 4. This assumption was based on both an increase in the number of Caterpillar engines sold to the Army, as well as potentially retrofitting other vehicles with TEG systems. The penetration curves for both market segments are shown in Figure 10.

Figure 10. TEG market penetration curves for the on-highway truck market and early adopter market such as Army vehicles market

For modeling the costs associated with the assembly process in the DCF model, it was assumed that the facility and capital required for fabricating 66,000 TEG units would be procured prior to year 1 of production. The logic behind this assumption was that the manufacturing process was more labor intensive than capital intensive. It made more sense to establish a facility and commit the capital at the onset rather than increasing the facility size and procuring new capital on an annual basis to reduce the contribution of capital depreciation on the overall costs. In this

case, the production capacity growth would be met by simply increasing the labor count and number of shifts

The optimized result from the DCF model based on the input data and assumptions listed above showed that in order to breakeven at year 6, the minimum TEG selling price to the on-highway truck market would have to be \$2,540, which translates to a selling price per watt of \$0.51. Detailed results of the DCF model are shown in Figure 11.

Volume and Labor Inputs		YEAR 1	YEAR 2	YEAR 3	YEAR 4	YEAR 5	YEAR 6
Units of TEG per year for On-Highway		0.0	0.0	0.0	8,800.0	39,000.0	61,000.0
Units of TEG for Army		1,100.0	2,200.0	4,400.0	4,400.0	5,000.0	5,000.0
Total Units Manufactured		1,100.0	2,200.0	4,400.0	13,200.0	44,000.0	66,000.0
Costs per watt		YEAR 1	YEAR 2	YEAR 3	YEAR 4	YEAR 5	YEAR 6
Electric Power Per generator (watts)		5,000	5,000	5,000	5,000	5,000	5,000
Thermoelectric Module Costs (\$/watt)		6.70	4.47	2.75	0.98	0.32	0.15
Heat Exchanger Costs (\$/watt)		0.17	0.14	0.12	0.10	0.08	0.06
Power Electronics Costs (\$/watt)		0.30	0.24	0.19	0.15	0.12	0.10
Other Material Expenses (Consumables) (\$/watt)		0.02	0.02	0.02	0.02	0.02	0.02
Costs Per Generator in Thousands \$		YEAR 1	YEAR 2	YEAR 3	YEAR 4	YEAR 5	YEAR 6
Thermoelectric Modules Cost Per Generator	\$	33.50	22.35	13.75	4.90	1.60	0.75
Heat Exchanger Costs Per Generator	\$	0.85	0.72	0.61	0.52	0.39	0.29
Power Electronics Costs Per Generator	\$	1.50	1.20	0.96	0.77	0.61	0.49
Other Material Expenses (Consumables) Per Generator	\$	0.08	0.08	0.08	0.08	0.08	0.08
Sell Price Per Generator in Thousands of \$'s		YEAR 1	YEAR 2	YEAR 3	YEAR 4	YEAR 5	YEAR 6
Selling Price Per Generator For On Highway-Market		0.00	0.00	0.00	2.54	2.54	2.54
Selling Price Per Generator For Army		30.00	25.00	20.00	3.18	3.18	3.18
Revenues in Thousands of \$'s		YEAR 1	YEAR 2	YEAR 3	YEAR 4	YEAR 5	YEAR 6
Sales for On-Highway Market at X/Unit		0.0	0.0	0.0	22,352.0	99,060.0	154,940.0
Sales for Military Market at X/Unit		33,000.0	55,000.0	88,000.0	13,970.0	15,875.0	15,875.0
Total Revenues in Thousands of \$'s		33,000.0	55,000.0	88,000.0	36,322.0	114,935.0	170,815.0
Expenses in Thousands of \$'s		YEAR 1	YEAR 2	YEAR 3	YEAR 4	YEAR 5	YEAR 6
Cost of Sales		0.0	0.0	0.0	0.0	0.0	0.0
Labor		280.8	374.4	468.0	936.0	2,808.0	4,118.4
Overhead including utilities		98.3	131.0	163.8	327.6	982.8	1,441.4
Occupancy per sq ft		52.6	52.6	52.6	52.6	52.6	52.6
Annual Thermoelectric Module Costs		36,850.0	49,170.0	60,500.0	64,680.0	70,400.0	49,500.0
Annual Heat Exchanger Costs		935.0	1,589.5	2,702.2	6,890.5	17,226.2	19,379.5
Annual Power Electronics Costs		1,650.0	2,640.0	4,224.0	10,137.6	27,033.6	32,440.3
Annual Other Material Expenses (Consumables)		82.5	165.0	330.0	990.0	3,300.0	4,950.0
Total Expenses in Thousands of \$'s		39,949.1	54,122.5	68,440.5	84,014.2	121,803.2	111,882.2
		YEAR 1	YEAR 2	YEAR 3	YEAR 4	YEAR 5	YEAR 6
Total Expenses+Depretiation+Inflation \$1000		\$ 40,320.37	\$ 55,230.92	\$ 70,375.13	\$ 87,142.76	\$ 127,489.65	\$ 118,284.31
Cost/5kW Generator		\$ 36,654.88	\$ 25,104.97	\$ 15,994.35	\$ 6,601.72	\$ 2,897.49	\$ 1,792.19
Cost \$/Watt		\$ 7.33	\$ 5.02	\$ 3.20	\$ 1.32	\$ 0.58	\$ 0.36
Selling Price Per On Highway Generator		\$ -	\$ -	\$ -	\$ 2,540.00	\$ 2,540.00	\$ 2,540.00
Selling Price Per Army Generator		\$ 30,000.00	\$ 25,000.00	\$ 20,000.00	\$ 3,175.00	\$ 3,175.00	\$ 3,175.00
Selling Price Per Watt On-Highway		\$ -	\$ -	\$ -	\$ 0.51	\$ 0.51	\$ 0.51
Selling Price Per Watt Army		\$ 6.00	\$ 5.00	\$ 4.00	\$ 0.64	\$ 0.64	\$ 0.64
Total After Tax Cash Flow (\$1000)		\$ (5,464.87)	\$ (4,800.96)	\$ 7,711.29	\$ (22,849.21)	\$ (27,261.85)	\$ 11,372.99

Figure 11. Discounted cash flow model results for the TEG

The contribution of each of the TEG system components to cost was analyzed on a year-by-year basis as shown in Figure 12 (a)-(f). The analysis shows that the cost of the thermoelectric devices was the largest contributor to the overall cost of the TEG system throughout all the years. However, the cost significantly drops as volumes picks up during the later years. The second cost contributor was the power electronics costs followed by the heat exchanger costs.

Figure 12. Contribution of each subsystem component to the overall cost of the TEG system for years 1 through 6 (a)-(f)

Comparing the minimum selling price of the TEG system to the maximum acceptable price, based on the market analysis, indicates that the TEG system is commercially viable for the on-highway truck market (see Figure 13). It is worth noting that the expected increase in the cost of diesel fuel was not factored in this analysis. Additionally, the payback period was assumed to be two years. The acceptable payback period for customers can and does vary. Both of these factors would increase the maximum acceptable market price considerably. A marketing strategy should focus on targeting customers that log a higher number of miles per year, and/or customers who own their trucks longer than average and, therefore, are willing to accept a longer payback period.

Figure 13. A comparison between the maximum acceptable purchase \$/watt to the minimum acceptable selling \$/watt for the TEG system for both the on-highway truck market segment and an early adopter market segment

2.5 Task 1.5 – Phase II Preparation

In preparation for Phase II, detailed Level II plans were generated, which include detailed technical paths and schedules based on the results from Phase I. UTRC has purchased the necessary equipment to fabricate and process the thermoelectric quantum well nanocomposites during Phase II using UTC dollars. In addition, the necessary ZT testing equipment has been purchased using UTC dollars. This equipment is expected to arrive at UTRC by September 2005. Three labs have also been renovated at UTRC - two for material fabrication and one for ZT property testing. Pratt & Whitney has developed schematics for the modifications of the cathodic arc equipment that will be used to deposit the quantum well materials and detailed costs have been received for the modification.

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**“Cost-Effective Fabrication Routes for the Production of Quantum Well Structures
and Recovery of Waste Heat from Heavy Duty Trucks”**

End of Budget Period 2
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1. EXECUTIVE SUMMARY

The primary objectives of Phase 2, Budget Period 2 were to: (a) demonstrate high ZT performance of QW films on Kapton[®] at the size required for a waste heat recovery generator or demonstrate 5% thermal-to-electrical conversion efficiency and (b) fabricate QW materials as heterogeneous nanocomposites that are deemed high enough quality to warrant ZT measurements and report a first set of ZT measurements for heterogeneous nanocomposites. A summary of the accomplishments made during Phase 2, budget period 2 are given below:

- A new TEG design was developed that resulted in a 6.5 – 7.0% fuel economy improvement, versus the earlier reported 4 – 4.5% (both taking into consideration benefits from the More Electric Truck design)
- A thermoelectric conversion efficiency rig was designed, fabricated, assembled, and validated using a Bi₂Te₃ couple. The design, instrumentation, operating procedures, and calculation assumptions and approaches were reviewed by JPL.
- Two Quantum Well (QW) film couples were assembled and data for Seebeck coefficient, electrical resistivity, and conversion efficiency were acquired.
- The Kapton[®]/Si/Si_{0.8}Ge_{0.2} QW couple exhibited very high electrical resistivity and gave a Seebeck coefficient that was low for QW films, but consistent with bulk values. The measured conversion efficiency was very low.
- The Kapton[®]/Alternate material couple also exhibited very high electrical resistivity and gave a Seebeck coefficient that was low for QW films, but consistent with bulk values. The measured conversion efficiency was also very low.
- Two routes for silicon germanium heterogeneous nanocomposites were identified: (a) hot pressing of Si nanoparticles into a coarse Si_{0.8}Ge_{0.2} powder mixture to form (Si)_x/(Si_{0.8}Ge_{0.2})_{1-x} and (b) arc melting of a uniformly mixed, pre-consolidated powder mixture of Si, Ge, and an additive phase, A, to form (A)_x(Si_{0.8}Ge_{0.2})_{1-x}.
- Hot pressing yielded samples that had densities ranging from 90 – 95% of theoretical, while arc melting yielded samples that had densities ranging from 85 - 100 % of theoretical.
- First TE property measurements were acquired for both silicon germanium heterogeneous nanocomposites. ZT values for the (Si)_x/(Si_{0.8}Ge_{0.2})_{1-x} heterogeneous nanocomposites formed by the hot pressing ranged from 0.17 – 0.21 at 175°C. These values are comparable to bulk silicon germanium. ZT values for undoped (A)_x(Si_{0.8}Ge_{0.2})_{1-x} heterogeneous nanocomposites, formed by hot pressing, ranged from 0.01 – 0.04 at 175°C. These values are significantly lower than fully doped, bulk silicon germanium, however comparable to the undoped, bulk silicon germanium sample prepared for the purpose of comparison.
- A phenolic resin was successfully demonstrated as a suitable carbon source to generate nanostructured boron carbide in-situ via reaction with amorphous boron powder.
- Formation of boron-rich boron carbide was demonstrated via direct reaction of B₄C with additional amorphous boron.
- Hot pressed boron carbide heterogeneous nanocomposites had densities that ranged from 77 to 97% of theoretical, with retained nanocrystallinity between 45 – 100 nm.
- First TE property measurements were acquired for the boron carbide heterogeneous bulk nanocomposites up to 400°C. Results were consistent with bulk thermoelectric properties.

After the Budget Period 2 review on October 10th, 2006, the DOE elected not to continue with this program.

2. BUDGET PERIOD 2 TECHNICAL PROGRESS

2.1 Improved Thermoelectric Generator (TEG) Design

The system level analysis carried out during Phase I of this program yielded a TEG design with a projected fuel economy improvement of 2.2% (4–4.5% taking into consideration benefits from the More Electric Truck (MET) design). In an effort to achieve a higher projection for fuel economy improvement, a small effort was made during this budget period to reevaluate the assumptions supporting the Phase I TEG design. After considering all parameters, the TEG was moved upstream to a hotter location in the exhaust and a dedicated cooling loop was included, resulted in a 4.4 % fuel economy improvement (6.5–7.0% taking into consideration benefits from the MET design). Considering future identified improvements in heat exchanger technology (including heat exchanger materials), up to 7% fuel economy improvement is now projected as achievable (9–9.5% taking into consideration benefits from the MET design).

2.2. Thermoelectric Conversion Efficiency Rig

The team's major milestone, at the end of budget period 2, is the successful demonstration of 5% conversion efficiency using a QW p-n couple. In order to satisfy this milestone, a thermoelectric conversion efficiency rig was needed. Efforts were therefore dedicated this budget period to the design, fabrication and assembly of such a rig. The test sample required for this rig was notably larger than the single, flat p-n couple demonstrated in the past by Hi-Z to give 12% conversion efficiency. The test sample also needed to be made consistent with the device design selected as part of Phase I. It was recognized that this larger test sample will have more thermal and electrical losses, when built for the first time, than the previous, single p-n couple. Consequently, a lower conversion efficiency milestone of 5% was set for the end of budget period 2. Also, before tests could be run using quantum well couples, the rig needed to be qualified using commercially available thermoelectric material. The following sections describe the final conversion efficiency rig, built as part of budget period 2, as well as the major steps taken to achieve a fully qualified state.

2.2.1 Heater Design

The thermoelectric conversion rig consists of 4 components: (1) a heater, (2) a Lavite structure, (3) a vacuum chamber, and (4) a Faraday cage. Of these, the most critical component is the heater, since its design significantly impacts the amount of heat entering the sample. The team went through several iterations before reaching agreement on a final heater design. Figure 1A shows a graphical representation of the final heater design.

To qualify the performance of the thermoelectric conversion rig, a Bi_2Te_3 test sample (P-N couple) was built, as shown in Figure 1B. This sample sized was chosen to match the thermal conductance of the P and N-type QW film samples to be fabricated. The P and N-legs were separated from one another, along their length, by placing a strip of Kapton[®] between them.

Figure 1. (A) Drawing of the thermoelectric conversion efficiency rig heater design showing dimensions and thermocouple placement on the hot side of the rig, (B) CAD model of the Bi_2Te_3 test sample (p-n couple) in the heater (thickness is exaggerated for the stainless steel heater strip)

To insert the sample into the rig, the cold side of the sample is clamped between two copper blocks by plastic screws. These copper blocks act as a cold sink to help draw the heat out of the test sample and provide electrical contacts to each leg of the sample. Contacts to the sample legs are made using an InGa eutectic solder which is rubbed on both the copper cold side blocks and the two ends of the sample. A thermocouple is then embedded in one of the copper pieces to measure the cold side temperature of the sample. The heater, quartz clamp, and copper contacts are then positioned within the Lavite structure, shown in Figures 2A and B.

Figure 2. (A) Front view of the thermoelectric sample (p-n couple) clamped in the thermoelectric conversion efficiency rig, (B) Side view of the thermoelectric sample (p-n couple) clamped in the thermoelectric conversion efficiency rig, and (C) conversion efficiency rig positioned inside the vacuum chamber

The Lavite structure provides strength to the TE conversion efficiency rig and allows for the necessary handling when samples are inserted or removed. Once the test sample is positioned within the TE conversion efficiency testing rig, a thermocouple is attached to the hot side of the sample with ceramic cement. Thermocouple tie-down points and connectors are then integrated with the Lavite structure to provide robust connection points for all of the thermocouple wires.

The thermoelectric conversion efficiency rig is then placed in a vacuum chamber, shown in Figure 2C, to minimize heat losses due to convection during test. The pressure inside the vacuum chamber during test is kept at less than 5×10^{-5} torr. In order to completely eliminate any EMI issues, a copper screen Faraday cage was installed around the vacuum chamber.

2.2.2 Rig Instrumentation

The various instruments used to operate and take measurements from the thermoelectric conversion efficiency rig are shown in Figure 3. The heater strips are connected to a variable DC source (label A). A digital voltmeter (label B) is used for all electrical measurements and a switchbox (label C) is used to select which voltage reading is displayed. The voltmeter is connected across a resistor (label D) to measure the electrical current applied to the thermoelectric conversion efficiency rig heater.

A switch is connected to the current source that can be used to quickly alternate the polarity of the applied heater current. A digital thermocouple meter (label E) is used to measure the temperature reading at each thermocouple. A dial (7 positions used, label F) selects which thermocouple reading is displayed. The heater voltage is measured by short circuiting, together, the leads from a thermocouple spot welded at one end of the heater and measuring the voltage between these two shorted junctions. The cold side copper contacts of the testing rig are connected to the voltmeter and to an external connection point where an electrical load can be applied to the thermoelectric couple being tested. A copper wire connects the thermoelectric conversion efficiency rig vacuum system baseplate to the grounding rod in the test laboratory.

Figure 3. Vacuum chamber and instruments used to measure temperatures and electrical inputs and outputs

2.2.3 Test Procedure

This section outlines the procedure used to gather the raw data from the thermoelectric conversion efficiency rig as well as the procedure used to process this raw data into a final value for conversion efficiency. For the purpose of illustration, the test data gathered from the Bi_2Te_3 test sample (P-N couple) is provided as the context throughout this section.

2.2.3.1 Raw data collection

The stepwise process to gather raw data from the thermoelectric conversion efficiency rig for both the Bi_2Te_3 test sample and the quantum well film samples is given below.

1. First, the heater is excited with a DC current supply. The supply is adjusted to maintain the hottest measured heater temperature at 250°C .
2. Once the temperatures within the system reach equilibrium, the heater current, heater voltages, heater temperatures, sample voltage, and sample temperatures are recorded.
3. The polarity of the heater current is switched to check for problems with the spot-welded thermocouple readings.
4. Next, a variable resistor is connected to the sample. For the Bi_2Te_3 test sample, the resistance is adjusted to a point where the sample produces half of its open-circuit

- voltage. This resistance corresponds to the point of highest efficiency and maximum power output.
5. Since the small amount of current flowing through the thermoelectric sample causes it to pump some additional heat from the hot side to the cold side, the system is allowed to equilibrate at a new temperature before the voltage and temperature readings are recorded again.
 6. At the completion of the test, the variable resistor is disconnected from the system and its value is measured and recorded.

The performance of the QW film sample is determined over a range of resistances since the maximum efficiency does not occur at matched load due to the higher ZT. Thus, the maximum efficiency occurs at a load ratio given by:

$$R_{\text{load}} = R_{\text{module}} * \sqrt{Z * (T_{\text{h}} + T_{\text{c}})/2 + 1}^{\text{[ref 1]}} \quad (\text{eq. 1})$$

2.2.3.2 Efficiency Calculations

The Seebeck coefficient, electrical resistivity; and the conversion efficiency are all determined using the experimental data gathered in section 2.2.3.1. Example data and calculations are outlined in Tables 1 and 2. The experimentally measured quantities are assigned a variable to denote that they are experimental data. Any property that was not directly measured, but rather calculated, is listed in the table followed by the relevant equation or equations. Results for a Bi_2Te_3 are being used to illustrate the procedure

Table 1. Calculations of Resistivity for Bi_2Te_3 Test Samples

Thickness of Each Bismuth Telluride Leg (t)	15 Mil	3.81E-04 M
Length of Each Bismuth Telluride Leg (L)	1.6 Cm	0.016 M
Width of Each Bismuth Telluride Leg (w)	0.22 In	0.0056 M
Matched Load Resistance of Bismuth Telluride Couple (R)		0.195 Ohm
Resistivity = $R \cdot A / L = R \cdot w \cdot t / (2 \cdot L)$		1.297E-05 Ohm-m

Values for ZT, shown in Table 2, are calculated from thermoelectric efficiency equation, where the average temperature is given by $T = (T_{\text{h}} + T_{\text{c}}) / 2$ and all temperatures are in Kelvin.

$$\text{Efficiency } (\eta, \%) = \Delta T / T_{\text{h}} * (\sqrt{1 + ZT} - 1) / (\sqrt{1 + ZT} + T_{\text{c}} / T_{\text{h}}) \quad (\text{eq. 2})$$

Table 2. Summary of data and calculation results from efficiency tests

Sample Tested in Efficiency Rig	Bi_2Te_3	Bi_2Te_3
Sample Circuit Condition	Open	Loaded
Measured Heater Current (I_{h} , Amps)	1.092	1.092
Measured Heater Voltage (V_{h} , Volts)	0.472	0.471

Measured Sample Hot Side Temperature (T_h , C)	178.4	168.9
Measured Sample Cold Side Temperature (T_c , C)	33.5	35.1
Measured Temperature Difference ($\Delta T = T_h - T_c$)	144.9	133.8
Measured Sample Open Circuit Voltage (V_o , Volts)	0.0476	
Measured Sample Loaded Voltage (V_L , Volts)		0.0215
Measured Resistance of Load (R_{Load} , Ohms)		0.1236
Measured Internal Resistance of Testing Rig (R_{rig} , Ohms)		0.073
Combined Resistance of Rig and Load ($R_L = R_{rig} + R_{Load}$, Ohms)		0.1966
Calculated Gross Heater Power ($Q = V_h I_h$, W)	0.516	0.515
FEA Calculation of Heat into Sample (Q_{in} , W)		0.087
FEA Calculation of Average Heat Through Sample (Q_{ave} , W)		0.052
Calculated Seebeck Coefficient ($S = V_o / (T_h - T_c)$, V/K)	3.28E-04	
Calculated Sample Power ($P_{out} = V_L^2 / R_L$, W)		2.35E-03
Resistivity (Shown Tbl. 2, Ohm-m)		1.31E-05
Gross Efficiency ($= P_{out} / Q$, %)		0.46
Corrected Efficiency ($= P_{out} / Q_{ave}$, %)		4.5
Calculated ZT from Gross Efficiency		0.053
Calculated ZT from Corrected Efficiency		0.685

2.2.3.2.1 Calculation of Heat In

A finite element thermal analysis was conducted on the thermoelectric conversion efficiency rig with a Bi_2Te_3 sample. The temperature measured on the cold side of the sample and at the outer ends of the heater wires were used as boundary conditions for the analysis. The quartz clamp surfaces, the copper wires, and the Bi_2Te_3 surfaces were assigned emissivity values and radiated to an environment at 30°C. An amount of heat equal to that recorded during the experiment was input into the heater strips. The thermal contact resistances between the surfaces in the model were set so that the temperature distribution on the heater and the sample hot side closely matched the measured temperatures. From the results of the analysis, a number of evenly spaced data points were taken on a cross section where the highest calculated heat flux within the Bi_2Te_3 was found near the hot side of the sample. One such data point is shown in Figure 4A. The average heat flux from all of these data points was found, and by multiplying by the cross sectional area of the Bi_2Te_3 legs, the heat flowing through the hot end of the sample was calculated. The numerical data labeled in Figure 4B can be simplified into two heat balances, see Table 3.

Figure 4. (A) Cross-section of the thermal analysis results showing heat flux through Bi_2Te_3 sample (single data point is shown near the hot side of the test sample) and (B) Heat Flow Schematic of Bi_2Te_3 Sample in Efficiency Testing Rig. Colors Indicate Heat Flux, W/m^2

Table 3. Summary of heat balance equations

Heater Heat Balance	Sample Heat Balance
Heater + Wire = Rig Radiation + Heat into Sample + Copper Wire	Heat into sample = Heat radiated + Heat out of sample + Heat converted
520mW + 190mW = 440mW + 90mW + 180mW	87 mW = 46 mW + 39 mW + 2 mW
710 mW = 710 mW	87 mW = 87 mW

2.3.2.2. Comparison of New Experimental Data with Previous Data

Table 4 gives the property data for the Bi_2Te_3 test sample (P-N couple) using the thermoelectric efficiency rig, and compares it to previous data for this material over the same temperature range. The previous data for the large temperature ranges present in the conversion efficiency rig were generated by taking the mean of the literature values at the hot and cold side temperatures. The Bi_2Te_3 experimental data measured in the conversion efficiency rig were in very good agreement with the previous data for that material. This good agreement demonstrates that the conversion efficiency rig can be used to accurately measure the Seebeck coefficient, electrical resistivity, and conversion efficiency of thermoelectric materials joined together into a couple with the proper dimensions and electrical contacts.

Table 4. Comparison of experimentally measured α , ρ , and calculated η values compared to previous data for the Bi_2Te_3 test sample

	Conversion Efficiency η , %	Seebeck Coefficient, S , $\mu\text{V/K}$ (for couple)	Electrical Resistivity ρ , ohm-m
Calculated from measurements	4.5	340	1.3×10^{-5}
Calculated from previous data	4.6	365	1.33×10^{-5}
Percent Difference	2.0	6.8	1.9

2.3. Quantum Well Film Fabrication

2.3.1 Buffer Layer Development

The first step in building a quantum well (QW) test couple, involving Kapton[®] as the substrate, is the deposition of a 1 micron or less buffer layer. This buffer layer must crystallographically match the structure of the QW films being deposited, which in this case are Si and $\text{Si}_{0.8}\text{Ge}_{0.2}$. The preferred choice for the buffer layer is therefore Si. The other critical feature of this buffer layer is that it must exhibit short range order. Once the short range order is verified in the buffer layer, the $\text{Si}/\text{Si}_{0.8}\text{Ge}_{0.2}$ QW films can be grown with the same crystallographic signature.

2.3.1.1 Silicon Buffer Layer

Prior to preparing full composite samples (buffer layer + QW layers), a series of “buffer layer only” samples (1 μm of Si on Kapton[®]) were prepared and characterized. Five different buffer layers samples were produced, each by magnetron sputtering, at five different substrate temperatures. The objective of this study was two-fold: (i) to select the optimum deposition temperature and (ii) to ensure that the buffer layer contains all of the above mentioned criteria. The Kapton[®] substrates were each 5-mils thick (127 μm) and were supplied to PNNL by Hi-Z. In an effort to minimize distortions within the Kapton[®] substrate, the Si layers were deposited on both sides of the substrate at substrate temperatures ranging from 325 to 425 °C. The Si layers were deposited as specified by the Hi-Z recipe. The substrate temperature was measured using a thermocouple placed at the surface of the substrate. Table 5 shows sample numbers and substrate temperatures. Evidence of short range order, as determined by Hi-Z using Auger Electron Spectroscopy (AES), is also listed.

Table 5. Si/Kapton® samples produced by PNNL and measured by Auger Electron Spectroscopy at Hi-Z

Sample No.	Si Thickness (μm)	T _{substrate} (°C)	Short range order (AES)	Comments
Si 3F-S	~1	325	No	
Si 3G-S	~1	350	No	
Si 3H-S	~1	375	No	
Si 3I-S	~1	400	No	Coated 2 sides
Si 3L-S	~1	425	No	Coated 2 sides

In addition to Auger analysis, these buffer layer samples were measured for thermoelectric properties, specifically power factor, α^2/ρ , where α is the Seebeck coefficient and ρ is electrical resistivity. Overall, these films showed lower than desirable power factor values even after annealing. The power factor was on the order of < 30 W/m-K (at 300K) and ρ was on the order > 1 ohm-cm. This very high electrical resistivity indicates little to no structural ordering in the microstructure. Target values are closer to 14.85 W/m-K and 2 mohm-cm

In addition to the lack of short range order, the films deposited at 400°C experienced an additional complication. The Auger data indicated the presence of oxygen, which can give rise to high electrical resistivity. While the exact source of oxygen is unknown, but believed to be coming from one of three sources: (1) the Kapton® film itself as expelled oxygen (e.g., scavenged), (2) the Kapton® film as expelled moisture (e.g., entrapped from original swollen film), or (3) inadequate vacuum in the sputtering chamber. To eliminate this concern, an outgassing step was introduced into the process before silicon deposition.

In addition to thermoelectric properties, mechanical stress was qualitatively evaluated on these buffer layer samples. Mechanical stress can easily distort the thin Kapton® substrate and render the sample useless for integration into a TE device. Figure 5 shows side views of the Si/Kapton® samples with one and both sides coated. Significant bending is observed for the sample coated on one side. This mechanical stress is eliminated for the sample coated on both sides.

Figure 5. Side view of Kapton® substrate coated on one side and both sides with 1 μm of Si

2.3.1.2 Sputtering Mask Assembly

Parallel to buffer layer studies in Section 2.3.1.1 a mask was fabricated at Hi-Z for the sputtering of QW films on both sides of Kapton® substrates, see Figure 6A. This mask importantly allows the substrate to be kept under tension. Figure 6B shows a representative sample prepared using this new mask. Hi-Z prepared the following samples using this new deposition assembly:

Figure 6. (A) Design drawing of the stainless steel mask for sputtering of three samples. (B) Representative sample (Si buffer layer on Kapton® substrate) obtained using designed mask.

- (1) P-type Si buffer/Kapton®
- (2) N-type Si buffer/Kapton®

The objective of this study was to assess whether or not material fabricated using this new sputter mask was crystalline. Auger data was collected for one of these samples and are given in Figure 7A. These data suggest a lack of crystallinity in the sample, as indicated by the large noise

compared to spectra for a known crystalline sample (Figure 7B).

Figure 7. (A) Auger Electron Spectroscopy (AES) of a Si buffer layer sample deposited at 350°C on Kapton®. The electrical resistivity of this sample was very high ($> 1 \text{ ohm-cm}$). The AES of Si buffer layer is shown. The large noise (oscillations around zero) is an indication of the amorphous structure in the film. (B) AES of a previous, Hi-Z Si/Kapton® film deposited at 325°C which showed a crystalline structure.

2.3.1.3 Laser Annealing

To overcome the challenge of achieving a crystalline buffer layer on Kapton® substrate, efforts were next focused on the evaluation of laser annealing at Caterpillar as a technique to induce short range order into the already deposited buffer layer samples. The original samples lacking short range order were sent to Caterpillar for laser annealing. Resistance measurements were made on the film both before and after laser annealing. The results obtained were encouraging. The laser annealed sample gave a 5,000x reduction in resistance compared to before laser annealing. The resistance after laser annealing, however, was still high. Microscopic cracking was also observed on this sample (see Figure 8A). To eliminate this cracking, a repeat run was performed with a lower laser power density. In this case, the microcracking was eliminated (see Figure 8B), however, the resistance was only reduced by 200x.

Figure 8. Optical images of films processed by laser annealing at Caterpillar. (A) Last set at high power density, giving microcracked films. (B) Laser set at low power density.

2.3.1.4 Modified Deposition/Heater Assembly

To further address the challenge of achieving a crystalline buffer layer of silicon on a Kapton[®] substrate, a root cause analysis was conducted within the team to determine possible causes for the poor performance. The sputtering conditions used for deposition of the Si/Si_{0.8}Ge_{0.2} QW films on a Kapton[®] were compared to past sputtering conditions to determine any differences. The temperature of the Kapton[®] substrate was also directly measured, before and during the sputtering process. A finite element thermal analysis was also performed on the deposition assembly and compared with the measured Kapton[®] temperatures.

One major difference between the previous and current Si/Si_{0.8}Ge_{0.2} QW films deposited on a Kapton substrate was the size and shape of the deposition area. For this program, the deposition region consisted of 3 rectangular strips that were each 0.5cm by 1.5cm. Figure 9A shows the entire deposition assembly with the 3 rectangular strips.

Figure 9. (A) 3 Strip Deposition Assembly, (B) 26 Strip Deposition Assembly and (C) 26 Couple radial module, before the Kapton[®] is cut away from the inner/outer edges

Once these strips are successfully sputtered with Si/Si_{0.8}Ge_{0.2} QW films, the strips can be cut out from the surrounding Kapton[®] substrate and stacked together for use in the efficiency test. The previous deposition geometry consisted of 26 rectangular strips with a radial orientation that were each 0.188 cm by 0.5 cm (see Figure 9B). The deposition geometry shown in Figure 9B differs slightly from the actual deposition geometry. The legs are parallel to the radial direction from the center of the mask in Figure 9B but the legs were actually angled slightly in a spiral pattern originating from the center of the deposition assembly. This spiral pattern of deposited Si/SiGe QW films on a Kapton[®] substrate can be seen in Figure 9C. 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[®] substrate (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 9C).

The modeled deposition geometry with straight radial legs is assumed to be a good representation of the thermal characteristics of actual deposition geometry, since it has the same area of exposed Kapton[®] substrate in an almost identical geometrical pattern.

To determine the temperature of the Kapton[®] substrate during the deposition process, thermal calculations using the deposition geometries in Figures 9A and B were performed. The heater ring in contact with the outer edge of the deposition assembly was set at 325°C. The back surface of the deposition assembly absorbs heat via radiation from the heater surface, which was set at 325°C, and via heat conduction in the mask from the heater ring. The deposition assembly dissipates heat via radiation from its outer surface to an environment at 30°C. The resulting temperature distribution for the two deposition assemblies is given in Figures 10A and B.

Figure 10. Temperature distributions calculated for (A) the 3-strip (B) 26-strip deposition assembly

These two temperature distributions are very different, highlighting the fact that the surface of the Kapton[®] can vary depending on the deposition assembly. Maintaining the proper Kapton[®] substrate temperature during Si/Si_{0.8}Ge_{0.2} QW films deposition is critical to the recrystallization and short range ordering of the initial silicon buffer layer which is, in turn, is important for the deposition of high performing Si/Si_{0.8}Ge_{0.2} QW films.

To experimentally confirm these calculation results, the three strip deposition assembly was 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[®] substrate exposed areas. The heater was raised to 325°C using the 3 strip deposition assembly within the vacuum chamber. The measured temperature at the edge of the Kapton[®] substrate was significantly lower than the heater temperature (~100°C lower). In order to quickly compensate for the lower Kapton[®] substrate temperature, the heater set point temperature was increased to a point where the measured Kapton[®] substrate temperature was approximately 325°C. Si/Si_{0.8}Ge_{0.2} QW films were then deposited on the Kapton[®] substrate with the heater set point increased. Due to the large temperature gradient, however, significant portions of the deposition area were too hot for the Kapton[®]. Consequently, measurements with the QW films produced were not possible.

To decrease the temperature gradient within the deposition areas, a new deposition assembly was then designed and fabricated (shown in Figure 11A), allowing a piece of copper to be positioned

between the heater and the deposition assembly. This copper piece has a much larger contact area with the substrate heater and can better conduct heat to Kapton[®] substrate deposition areas. Figure 11B shows a design of the copper piece in contact with the heater, the substrate clamp, and the mask. Figure 11C shows a design of the copper piece in contact with the heater, the substrate clamp, the mask, and the region of the Kapton[®] substrate within the deposition area.

Figure 11. (A) Copper piece placed between the heater and the deposition assembly to provide better thermal contact between the heater and the substrate, (B) Copper in direct contact with substrate mask and substrate clamp and (C) Copper in direct contact with Kapton[®] substrate, mask, and substrate clamp

Cross-sectional views of the original design and the designs in Figures 11B and 11C are given in Figure 12. In the original design, heat is transferred to the Kapton[®] substrate deposition area by radiation from the heater and conduction from the heater edge to the clamp. This heat travels to the mask and then to the Kapton[®] substrate. In the Figure 11B design, heat is transferred to the Kapton[®] substrate deposition area by radiation from the copper and conduction from the heater edge. This heat travels first to the clamp and then to the mask and finally to the Kapton[®] substrate. In the Figure 11C design, heat is transferred to the Kapton[®] substrate deposition area by conduction from the copper to the Kapton[®] substrate. This design was selected as best, since it provides the best heat transfer from the heater, due to the large thermal conductivity of copper as well as the contact of the copper with the Kapton[®] substrate deposition area.

Figure 12. Cross-sectional views through the center of the Kapton[®] substrate deposition area

A finite element thermal analysis of the revised disposition/heater assembly was next conducted and the results are given in Figure 13A (Figure 11B design) and Figure 13B (Figure 11C design). For these analyses, the back of the modeled heater was held at 325°C and there was no radiation heat input at the back of the clamp since the copper plate was in contact with the clamp and

heater. The calculated results indicated the temperature of the deposition areas to be only 5°C to 10°C below the set point temperature of the heater. These results show that the new designs have considerably improved the thermal contact between the heater and the Kapton® substrate.

Figure 13. Calculation Results of the new deposition/heater assemblies (A) Copper Piece in Contact with Substrate Clamp and Mask (Figure 11B design), (B) Copper Piece in Contact with Kapton® Substrate, Substrate Clamp, and Mask (Figure 11C design).

Photographs of the downselected disposition/heater assembly with the new copper piece (Figure 11C design) and clamping assembly are shown in Figure 14.

Figure 14. Pictures of the revised deposition/heater assembly

Following completion of the deposition / heater assembly, two N-type QW films were sputtered at Hi-Z. The film thickness was 4 and 8 μm . Small angle X-ray diffraction measurements were acquired on the 4-micron film, prior to contact deposition, and the resulting structure was determined as amorphous. Contacts were deposited on the two films using magnetron sputtering. Seebeck and electrical resistivity measurements were acquired on the 8 micron sample and the results are given in Figure 15. The Seebeck coefficient was equivalent to bulk values for silicon germanium. The electrical resistivity, however, was very high. Consequently the power factor was significantly smaller than the target value of $\sim 15 \text{ W/m-K}$. It was concluded from these results that the modifications made to the deposition assembly were not sufficient to produce high performing QW films.

Figure 15. Electrical resistivity and power factor data on the first QW film samples prepared after modifications were made to the sputter heater / deposition assembly.

2.3.1.5 Lower Melting Point Buffer Layer

In an attempt to achieve a crystalline buffer layer (to support the growth of high quality QW films), the Si buffer layer was next replaced with a lower melting point buffer layer. The objective of using a lower melting buffer layer is to access crystallization temperatures closer to those applied during the deposition process or, subsequently, during the laser annealing process. To assess the feasibility of this concept, a 1.8 micron layer of the lower melting point element was deposited on Kapton®. Figure 16 shows the resulting Auger spectra.

Figure 16. (A) AES spectra of a Si buffer layer sample on Kapton®. (B) AES spectra of a lower melting point buffer layer sample on Kapton®.

Unlike the silicon buffer layer where a crystalline state was not achieved, these data suggest that a crystalline state can be achieved by laser annealing. This crystalline state is indicated by a reduced level of noise (oscillations) around the zero point. Si and $\text{Si}_{0.8}\text{Ge}_{0.2}$ QW films were then deposited on this lower melting point buffer layer. Room temperature electrical resistivity and Seebeck coefficient measurements are underway and will be reported in October.

2.4 Quantum Well Couple Assembly

The QW material required for the couple efficiency measurements was sputtered at PNNL, due to their larger sputtering machine capabilities. The following three couples were planned for assembly:

- *Kapton®/Si/($\text{Si}_{0.8}\text{Ge}_{0.2}$) couple*
- *Kapton®/Alternate material couple*
- *Kapton®/Lower melting point buffer layer/($\text{Si}_{0.8}\text{Ge}_{0.2}$) couple*

The following sections will describe the couple assembly process, the couples assembled, and the thermoelectric property data for the QW films couple that was used for conversion efficiency measurements.

2.4.1 QW Couple Assembly Process

The following section describes the three steps involved with assembling the QW films into the p-n couple: (1) film deposition, (2) laser cutting and (3) contact deposition.

2.4.1.1 Film Deposition

The film deposition process involves three steps: (1) sputtering of a buffer layer (if needed), (2) laser annealing the buffer layer (if needed), and sputtering of the QW films. The buffer layer and QW films were sputtered using an RF magnetron system. The coatings were deposited at 350C. A Kapton® sheet was placed in a sandwich-type holder that allows for deposition on each side of the substrate without removal from the holder. This approach reduces the handling and stress on the coatings. For each deposition run, two substrates were loaded to allow for spare segments and to enable thermoelectric property measurements to be made with a single segment.

2.4.1.2 Laser Cutting

Each of the P- and N-type QW films were then sectioned at PNNL into twelve smaller segments using the Resonetics Maestro Excimer Laser micromachining system process (see Figure 17A). Figure 17B shows one laser-sectioned segment that is 1.4cm x 0.5cm. The texture on the surface is due to the laser annealing of the Si buffer layer.

Figure 17. (A) Laser sectioning schematic (B) Laser sectioned segment

2.4.1.3 Contact Deposition

Several approaches were evaluated during this budget period for couple assembly. The following approach was downselected as the preferred approach. Prior to assembly into a couple, the edges of each individual segment were cleaned to remove any char residue left by the laser sectioning. Ten segments were then assembled, as shown in Figure 18A. Kapton® sheets were used to mask the stacked segments for contact deposition. Due to concerns around the outgassing of Kapton® tape, use of this tape was kept to a minimum during the contact deposition.

Figure 18. (A) Assembly and masking schematic. Practice piece assembled at PNNL.

In the same deposition run, one end of one N- and P-type assembly was coated with contacts. The assembly was then reloaded and the process repeated to coat the opposite end. Figure 19 shows the contact location on the thermoelectric material, while Figure 20 shows an example of a completed assembly.

Figure 19. Schematic highlighting the placement of contacts on the P-N couple

Figure 20. (A) QW stack assembly mounting station in preparation for contact material deposition, (B) QW stack assembly after contact material deposition – front on view. (C) QW stack assembly after contact material deposition – side view

2.5 QW Film Couple Testing

The following section describes the results of the data acquired using the thermoelectric conversion efficiency rig at Hi-Z for the following three couples:

- Si/Si_{0.8}Ge_{0.2} on a Si buffer layer on a Kapton® substrate
- Si/Si_{0.8}Ge_{0.2} on a lower melting point buffer layer on a Kapton® substrate
- P-type AgSbTe₂/GeTe, N-type AgPbTe/PbTe on Kapton® substrates

2.5.1 1st QW Film Couple – Kapton® /Si/(Si_{0.8}Ge_{0.2})

The N- and P-type Si/(Si_{0.8}Ge_{0.2}) QW films were deposited on Si buffer layers on both sides of a 5-mil Kapton® substrate. The P and N-type material consisted of 100 Angstrom, alternating layers of Si and SiGe, deposited by magnetron. P and N-type QW films were deposited to approximately a 10 micron thickness on each side. The laser cutting, couple assembly, masking, and contact deposition followed the same procedures outlined in Section 2.4.1. Prior to laser annealing this material, small angle X-ray diffraction data was collected in order to assess the degree of crystallinity, see Figure 21A. At this stage, the material lacked the necessary level of crystallinity. Figure 21B shows the same material, after laser annealing. The material still lacked the necessary level of crystallinity. As such, the conversion efficiency values were anticipated to be low.

Figure 21. Small angle X-ray diffraction data collected on the first QW Film Couple material - Kapton® /Si/(Si_{0.8}Ge_{0.2}) - (A) before laser annealing and (B) after laser annealing. Both spectra indicate an amorphous structure.

This material (N-type only) was also characterized for its thermoelectric properties, see Figure 22. The electrical resistivity values were very high. The Seebeck values were equivalent to bulk silicon germanium. This data agrees with the X-ray data shown above.

Figure 22. Temperature dependent Seebeck and Electrical resistivity values for the material (N-type Si/Si_{0.8}Ge_{0.2} on Si buffer layer on Kapton®) placed into the 1st couple for conversion efficiency testing.

Figure 23 shows the final, assembled couple before being placed into the conversion efficiency rig for testing.

Figure 23. Picture of the final, assembled first P-N couple for conversion efficiency testing - Kapton® /Si/(Si_{0.8}Ge_{0.2})

Test data were next acquired using the thermoelectric conversion efficiency rig at Hi-Z and consisted of Seebeck coefficient, electrical resistivity and conversion efficiency measurements. Table 6 shows the measured property values are compared with the previous data. The previous data for the QW materials came from previous thermoelectric property measurements made at Hi-Z of QW films deposited on silicon substrates. The QW films deposited on Kapton® substrates exhibited very low conversion efficiency, primarily due to the very high material electrical resistivity. Also, the electrical resistivity of the QW films measured in the efficiency rig decreased with increasing temperature, instead of increasing with increasing temperature as was expected from the previous data. The Seebeck coefficient was lower than expected for QW film material, but was consistent with a bulk material Seebeck

coefficient. X-ray data on this sample indicated that the QW film material was non-crystalline providing an explanation for the high electrical resistivity and low Seebeck coefficient. Despite these poor results, significant experience in assembling this 1st QW couple was gained as a result of completing these

Table 6. Comparison of experimentally measured α , ρ , and η with previous data

1 st QW Couple		Conversion Efficiency η , %	Seebeck Coefficient S , $\mu\text{V/K}$ (for couple)	Electrical Resistivity ρ , mohm-cm
Low Temperature	Calculated from previous data collected at Hi-Z (EXPECTED)	8.0	2,020	1.19
	New couple measurement (RESULTS)	3.8×10^{-4}	470	110,000
High Temperature	Calculated from previous data collected at Hi-Z (EXPECTED)	13.2	2,100	1.47
	New couple measurement (RESULTS)	8.8×10^{-4}	520	67,000

2.5.2 2nd QW Film Couple – Kapton® / lower melting point buffer layer / ($\text{Si}_{0.8}\text{Ge}_{0.2}$)

In an attempt to increase the probability of a crystalline buffer layer, a lower melting point buffer layer will be used for the 2nd Si/ $\text{Si}_{0.8}\text{Ge}_{0.2}$ QW couple. Justification for this buffer layer has been given in Section 2.3.1.5. This couple will contain 1 micron of the lower melting point buffer layer, deposited on both sides of a sheet of Kapton® with P and N-type Si/ $\text{Si}_{0.8}\text{Ge}_{0.2}$ QW films subsequently deposited to a thickness on each side of approximately 5 μm . The thickness of each Si and $\text{Si}_{0.8}\text{Ge}_{0.2}$ will be 100 Angstroms. Prior to depositing the QW films, the lower melting point buffer layer will be laser annealed. The laser cutting, couple assembly, masking, and contact deposition will follow the same procedures outlined in Section 2.4.1. This couple will be fabricated and assembled in October. Test data will be acquired by the end of November using the thermoelectric conversion efficiency rig at Hi-Z and will consist of Seebeck coefficient, electrical resistivity and conversion efficiency measurements.

2.5.3 3rd QW Film Couple – Kapton® / Alternate Material

To further increase the probability of successfully achieving the 5% efficiency goal by the end of budget period 2, a 3rd QW film couple using alternate thermoelectric materials was fabricated. The P and N-type materials consist each of 100 Angstrom of alternating layers of the select materials, deposited by magnetron sputtering on a sheet of Kapton®. P and N-type quantum well films were deposited to approximately 5 micron thickness on each side. The laser cutting, couple assembly, masking, and contact deposition followed the same procedures outlined in Section 2.4.1. This material (P-type only) was characterized for its thermoelectric properties, see Figure 24. The electrical resistivity values for this material were very high. The Seebeck values were equivalent to that expected for a bulk thermoelectric material. No significant enhancement due to a quantum well effect were observed. Figure 25 shows the final, assembled couple before being placed into the conversion efficiency rig for testing. Test data were next acquired using the thermoelectric conversion efficiency rig at Hi-Z and consisted of Seebeck coefficient, electrical resistivity and conversion efficiency measurements. Table 7 shows the measured property values. This couple exhibited very low conversion efficiency and very high electrical resistivity. The Seebeck coefficients were again lower than expected for QW film

material, but was consistent with a bulk material Seebeck coefficient and the electrical resistivity.

Figure 24. Temperature dependent Seebeck and Electrical resistivity values for the material (P-type on Kapton®) placed into the 3rd couple for conversion efficiency testing.

Figure 25. Picture of the final, assembled first P-N couple for conversion efficiency testing - Kapton® /Alternate Material

Table 7. Experimentally measured α , ρ , and η on the 3rd QW film couple

3 rd QW Couple		Conversion Efficiency η , %	Seebeck Coefficient S , $\mu\text{V/K}$ @ 113°C	Electrical Resistivity ρ , mohm-cm @ 113°C
TE Couple	Couple measurement	3×10^{-3}	323	146

2.6 Qualification of ZT Testing Equipment at UTRC

A further objective of this program is the evaluation of heterogeneous nanocomposites as an alternative path to high ZT material. Specifically, heterogeneous nanocomposites of silicon germanium and boron carbide are being investigated. To prepare for the TE testing of heterogeneous nanocomposites, the commercial ZT testing equipment that was acquired and setup during Phase I of this project (Figure 26) underwent qualification studies using known TE materials. The objective of these studies was two-fold: (1) to qualify the testing equipment against known thermoelectric materials such that there was confidence in the measurements with fabricated samples, and (2) to acquire relevant baseline data for the purpose of comparison against data obtained for the heterogeneous nanocomposites. The following section gives the results of these qualification/baselining studies.

Figure 26. *Left:* ULVAC-RIKO ZEM-2 electrical resistivity/seebeck measurement station ; *Right:* Anter Flashline 3000 thermal conductivity analyzer

2.6.1. Bulk Bismuth Telluride

The first qualification study was carried out at the lower temperature range using bulk bismuth telluride. Specimens of the necessary geometry (round shaped for thermal diffusivity and bar shaped for Seebeck and electrical resistivity) and type (P and N) were provided by Hi-Z. Data were obtained for both Seebeck coefficient and electrical resistivity from -100 to 25°C using the cryostat configuration and from 80°C to 250°C using the furnace configuration. Thermal diffusivity data were obtained from room temperature up to 250 °C and, together with data for specific heat capacity and density, were processed to give thermal conductivity. The data were then used to calculate ZT values as a function of temperature. The ZT value at room temperature was compared to the Hi-Z measured ZT at room temperature. Figure 27 gives the electrical resistivity, Seebeck, thermal conductivity and ZT data for both P and N-type samples. The agreement was very good for both electrical resistivity and Seebeck coefficient. The collected values for thermal conductivity and ZT were within reason, however, data was not able to be obtained at 25°C and so a direct correlation cannot be made. Overall, this data suggests that confidence can be placed behind future, fabricated TE samples.

Figure 27. Temperature dependent electrical resistivity, Seebeck, thermal conductivity and ZT data for N- and P-type Bi₂Te₃ sample collected at UTRC

2.6.2 Bulk Silicon Germanium

The second qualification study was performed using bulk silicon germanium. From this sample, two separate specimens were cut for testing. Seebeck coefficient and electrical resistivity measurements were obtained using a bar shaped sample and thermal conductivity was obtained using a disk shaped sample. Data for all three parameters were obtained from room temperature up to 450°C.

Figure 28 gives the measurement results. Unlike the Bi_2Te_3 specimens, TE property data were not available for the exact sample being measured, but a comparison was made with values obtained from the CRC Handbook of Thermoelectrics. The Seebeck coefficient, electrical resistivity, and thermal conductivity values were, on average, lower by 13% to that expected (standard deviation 0.9%), lower by 40% of that expected (standard deviation 2.0%), and within 0.1% of that expected (standard deviation 0.7%), respectively. The resulting ZT values were, on average, within 46% of that expected (standard deviation 16%). The ZT values for the specimen measured ranged from 0.13 to 0.71 as a function of temperature, compared to 0.09 to 0.59 (CRC Handbook) for the similar temperature range.

Figure 28. Baseline data for $\text{Si}_{0.8}\text{Ge}_{0.2}$; Comparison between data collected at UTRC and textbook values from the CRC handbook of thermoelectrics

2.7 Heterogeneous Nanocomposites

The following section describes the: (i) technical approaches evaluated and downselected to fabricate heterogeneous nanocomposites of silicon germanium and boron carbide, (ii) experimental work performed within budget period 2, and (iii) preliminary TE property results on the fabricated heterogeneous nanocomposites.

2.7.1 Silicon Germanium Nanocomposite

Preparation of bulk heterogeneous nanocomposites in the silicon germanium system was considered a potential low cost alternative to layered QW films. ZT values reported by Hi-Z for a layered Si/Si_{0.8}Ge_{0.2} QW material system, approximately 3.5 at 50 °C decreasing to nominally 3.4 near 200 °C, were used as target properties

During this budget period, two technical approaches were selected and pursued to fabricate silicon germanium based heterogeneous nanocomposites: (1) hot isostatic pressing (HIP) of commercial Si nanoparticles in coarse Si_{0.8}Ge_{0.2} to form Si/Si_{0.8}Ge_{0.2}, see Figure 29A, and (2) arc melting of silicon and germanium powders together with an insoluble additive phase to form bulk Si_{0.8}Ge_{0.2} matrix embedded with nanoscale inclusions, see Figure 29B. In both cases, the objective is the same: to significantly lower the thermal conductivity via phonon scattering mechanisms at the silicon - silicon germanium or additive - silicon germanium interface. More optimistically, the objective is to moderately enhance the Seebeck coefficient through quantum confinement of electrons or holes.

Figure 29. Targeted material micro-structures through (A) hot isostatic pressing, and (B) arc melting

2.7.1.1 Fabrication Approach #1 - Hot Isostatic Pressing

Figure 30 shows the process steps involved with fabrication approach #1. Silicon nanoparticles are first mixed with coarse Si_{0.8}Ge_{0.2} to achieve a powder mixture. This mixture is then placed inside a glass ampoule and flame sealed under vacuum. The ampoule is subsequently consolidated by hot isostatic pressing to a dense part. The glass is then removed from the part and the part is machined shapes appropriate for ZT testing.

To achieve the desired final state, several steps need to occur:

- Procurement of silicon nanoparticles
- Procurement of alloyed silicon germanium powder
- Selection and/or development of an appropriate mixing technique to achieve high (> 95%) silicon dispersion
- Identification of the proper HIP profile (time, temperature, pressure) that leads a highly dense part (> 95% theoretical) but at the same time retains the silicon nanostructure.

The silicon germanium powder was initially acquired from Plasmaterials and ACI alloys because these vendors provide the sputtering targets used by Hi-Z and PNNL for the fabrication of QW films. Once acquired, however structural (XRD) and thermal (DSC) characterization on this material determined that these materials were phase separated and not alloyed. In addition, the material obtained from ACI alloys contained large amounts of impurities. To correct this problem, the material provided by Plasmaterials was returned for reprocessing under more aggressive conditions. After reprocessing, the material was characterized again and found still to be phase separated. Both material suppliers were eliminated as a possible material source and Dr. Bruce Cook at Ames Laboratory was contacted as an alternate source for alloyed silicon-germanium powder. Ames Laboratory uses a mechanical milling approach to produce alloyed silicon-germanium powders [ref 1]. Test samples were acquired from Ames laboratory using two different mechanical milling processes – Spex mill and Zozz mill. Characterization data were collected on these materials at UTRC, leading to the downselection of Spex milling as the process to generate alloyed silicon germanium, and a batch of material was ordered from Ames Laboratory using this process for this effort.

Figure 31. Melt spun ribbons of silicon-germanium, produced by Ames Laboratory.

(calculated as $\text{Si}_{0.94}\text{Ge}_{0.06}$ by X-ray diffraction lattice constant), presumably due to the vaporization of germanium at the temperatures experienced during melting process. Consequently, this approach was deemed as not viable for generating alloyed silicon-germanium

Figure 30. Detailed process to achieving $\text{Si}/\text{Si}_{0.8}\text{Ge}_{0.2}$ as heterogeneous nanocomposites through hot isostatic pressing

As a risk reduction activity, Ames Laboratory was also requested to fabricate alloyed silicon-germanium powder using a melt-spin approach. This approach offers the advantage of starting from a completely homogenous, molten state of elements. It also avoids the problem of producing a phase segregated product because of the very fast quench rate established through the solidus-liquidus region in the phase diagram. The material was produced and is shown below in Figure 31. It is made up of ribbons and would require further processing before use to fabricate heterogeneous nanocomposite material.

X-ray data indicated that this material was germanium poor

Efforts also focused on selecting a proper mixing technique to provide high (> 95%) dispersion of silicon in the coarser silicon germanium powder. Prior to working with silicon as the nanoparticle phase, two preliminary studies were conducted in which a surrogate material was used. This surrogate material was necessary because silicon is very similar to $\text{Si}_{0.8}\text{Ge}_{0.2}$ compositionally. As such, it is more challenging to distinguish these two materials in the final heterogeneous nanocomposite using scanning electron microscopy (SEM) techniques.

The first step in choosing a proper mixing technique was to find the appropriate volume fraction whereby various mixing methods could be evaluated. To do this, silica (SiO_2) nanoparticles were mixed with silicon germanium coarse powders at various volume fractions. Based on visual examination of elemental oxygen maps, a 10% volume fraction was selected as the best. A second study was conducted in which the volume fraction was fixed at 10% and the mixing technique was varied. This time, aluminum nanoparticles (average particle size of 100 nm) were selected as the surrogate phase due to their greater compositional contrast against silicon germanium. Twelve different mixing methods were evaluated. The resulting powders were pressed into pellets, cross-sectioned and embedded in epoxy for microscopic evaluation. The objective of this study was to acquire aluminum maps for each sample using scanning electron microscopy (SEM) and use these maps to quantify an area % of aluminum detected. Because SEM cannot detect particles < 1 micron, an ideal case would be no aluminum detected, and any detected aluminum would indicate agglomeration. Figure 32 shows representative SEM images, while Table 8 gives the quantitative output.

Figure 32. SEM analysis of samples prepared as part of a mixing study; bright spots in (B) indicate the presence of aluminum

Table 8. Measured percent dispersion of aluminum nanoparticles in a coarse silicon germanium matrix.

Mixing Method	Area Fraction Detected (out of 10%)	Percent Dispersed (%)
1.	1.6	84
2.	2.1	79
3.	4.1	59
4.	3.3	67
5.	4.4	56
6.	4.9	51
7.	4.5	55
8.	4.6	54
9.	8.0	20
10.	3.3	67
11.	4.4	56
12.	5.9	41

Of the 10 volume percent aluminum nanoparticles added to the coarse silicon germanium powder, on average approximately 57% (ranging from 20 – 84%) was determined as

undetectable by SEM and therefore assumed as submicron in scale. The goal was to have 100% of aluminum nanoparticles undetectable by SEM. A value of 100% indicates a lack of agglomeration between particles and therefore good dispersion. The two best approaches gave approximately 80% dispersion.

Mixing methods #2, #10 and #11 were selected for further evaluation based on: (i) dispersion achieved, (i) number of variables available to optimize, and (iii) ease of method. A second set of optimization experiments was conducted as an attempt to increase the percent dispersion from 80% to closer to 100%. Aluminum maps were again collected and the area% detected was calculated. Method #2 gave a dispersion of 97%, method #10 gave a dispersion of 79% and method #11 gave a dispersion of 88%. Based on these results, method #2 was downselected as the preferred mixing method. The next step was the transfer of this mixing technique to the relevant Si / Si_{0.8}Ge_{0.2} powder mixtures and the fabrication of a series of heterogeneous nanocomposites for ZT testing. Using the process described above, one baseline Si_{0.8}Ge_{0.2} and five nanocomposite (Si)_x/(Si_{0.8}Ge_{0.2})_{1-x} samples were prepared. Table 9 gives the experimental data on these samples, including electrical resistivity, Seebeck coefficient, thermal conductivity and ZT at 175°C. ZT values on the samples measured to date ranged from 0.17 – 0.26 at 175°C. These values are comparable to bulk silicon germanium. The data outstanding will be collected and reported on in October.

Table 9. Experimental data for density, electrical resistivity, Seebeck coefficient, thermal conductivity and ZT*.

Sample	Atomic % Si Nanoparticles	Atomic % Si _{0.8} Ge _{0.2}	Percent Theoretical Density (%)	Electrical Resistivity (mohm-cm)	Seebeck Coefficient (μV/K)	Thermal Conductivity (W/m-K)	ZT
Baseline	0	100	96	1.74	-161	3.68	0.18
A	1	99	94	3.03	-180	2.75	0.17
B	2	98	▲	▲	▲	▲	▲
C	5	95	90	2.76	-177	2.41	0.21
D	10	90	▲	▲	▲	▲	▲
E	25	75	▲	▲	▲	▲	▲

* Data points taken at 175°C; ▲ data outstanding

Figure 33 shows temperature dependent ZT data for the baseline HIP sample compared to known, bulk ZT data for silicon germanium. The ZT data obtained on the baseline sample was equivalent to that reported in the CRC handbook of thermoelectrics and is slightly deteriorated compared to UTRC data on an Ames Laboratory sample. This suggests that the processing steps applied to the baseline powder do not significantly deteriorate the properties. Figure 33 shows next the ZT data for baseline HIP sample compared to the specimens containing Si nanoparticles.

The samples containing Si nanoparticles gave the desired effect of a thermal conductivity

Figure 33. Temperature dependent ZT data of the baseline HIP sample compared to bulk data (CRC Handbook , Ames ingot)

reduction (Figure 34A), however, the ZT values were roughly equivalent to that for the baseline sample (Figure 34B). This is due to the fact that the electrical resistivity was also increased.

Figure 34. (A) Temperature dependent thermal conductivity data for the samples containing Si nanoparticles compared to the baseline HIP sample. (B) Temperature dependent ZT data for the samples containing Si nanoparticles compared to the baseline HIP sample.

2.7.1.2 Fabrication Approach #2 - Arc Melting

As an alternative method to hot pressing, a second pathway was pursued in which a third element or mixture of elements was combined with coarse silicon and germanium powders, melted to a fully molten state using an arc melt, and then quickly quenched to room temperature. Figure 35 shows the process steps involved with this process. Retrieved solid ingots were cut to the appropriate shape for ZT testing. In the instance where the third element was highly sensitive to oxygen, the powder mixture was pre-consolidated using a cold isostatic press and then arc melted.

Two additive phases, A1 and A2, were selected for study, since their phase diagram information indicated that both are insoluble with silicon and germanium. A second selection criteria involved evaluation of the additive phase's physical properties. A1 exhibits very low electrical resistivity, which is desirable in order to minimize the amount of overall degradation to this parameter in the composite. In order to further minimize the negative impact on electrical resistivity, a "coherent" interface was targeted between the silicon germanium and the additive phase. A coherent interface means that the crystal structure and lattice parameter of the additive phase will match closely that of $\text{Si}_{0.8}\text{Ge}_{0.2}$. Adding this third criterion to the selection process led to A2.

Figure 35. Detailed process to achieving A/ $\text{Si}_{0.8}\text{Ge}_{0.2}$ as heterogeneous nanocomposites through arc melting

Fifteen mixtures of silicon, germanium and the additive phase, A1 or A2, were prepared, containing 1, 5 and 10 atomic % of the additives (Table 10). The effect of coarse powder versus nanopowder as the third phase on the final product was also investigated. Included in this study was also a baseline sample where no additive phase was introduced. An initial sample was sent to Michigan Tech University for arc melting in order to test the process (10 atomic % coarse A2 in 80/20 silicon germanium mixture) and to assess the feasibility of forming dispersed A2 nanoparticles inside a matrix of silicon-germanium.

Table 10. Powder compositions prepared by arc melting				
Additive Type	Additive Size	Additive Amount (atomic % added to 80/20 mixture of silicon and germanium)		
		1	5	10
A2	Coarse	X	X	X
	Nano	X	X	X
A1	Coarse	X	X	X
	Nano	X	X	X

Characterization data on this first arc-melted sample (X-ray diffraction, SEM, see Figure 36) indicated that A2 formed. All of the silicon and germanium powders were alloyed to the 80/20 phase, all of the additive phase in the powder reacted to form A2, and no other competing phases were detected. The A2 particles, however, were micron scale rather than the desired nano scale, suggesting that either the starting size of the additive phase should be smaller or the cooling rate within the arc melting process should be made faster.

Figure 36. X-ray diffraction and scanning electron microscopy data on collected on the first arc melted sample

Based on these results, a new batch of samples was submitted to MTU University for arc melting. The effect of the size of the additive phase was evaluated with this new batch of samples. Included in this new batch of samples was also a baseline silicon-germanium sample.

From this study, more characterization data was obtained and the following conclusions made:

- In all cases, the presence of A1 and A2 was verified
- In all cases, the silicon and germanium formed an alloy
- In all cases, micron sized particles of the desired additive phases were formed
- The size of the starting powder (nano vs. coarser) did not impact the resulting size of the

additive phase.

- To achieve the desired nano additive phase, a faster quench rate is likely necessary.

The samples that were of adequate size and shape (grey boxes highlighted above in Table 9) were then machined for ZT testing. Table 11 gives the experimental data obtained for density, electrical resistivity, Seebeck coefficient, thermal conductivity and ZT at 175°C.

Table 11. Experimental data for density, electrical resistivity, Seebeck coefficient, thermal conductivity and ZT*.

Sample	Description	Percent Theoretical Density (%)	Electrical Resistivity (mohm-cm)	Seebeck coefficient ($\mu\text{V/K}$)	Thermal Conductivity (W/m-K)	ZT
A	Ames Lab $\text{Si}_{0.8}\text{Ge}_{0.2}$ (baseline sample, doped)	94	0.67	-132	4.3	0.27
B	UTRC arc melted $\text{Si}_{0.8}\text{Ge}_{0.2}$ (baseline sample, undoped)	85	40	-701	10.9	0.05
1	$(\text{A2})_{0.01}(\text{Si}_{0.8}\text{Ge}_{0.2})_{0.99}$	89	15.2	294	7.5	0.03
2	$(\text{A2})_{0.11}(\text{Si}_{0.8}\text{Ge}_{0.2})_{0.90}$	100	16.9	150	7.7	0.01
3	$(\text{A1})_{0.1}(\text{Si}_{0.8}\text{Ge}_{0.2})_{0.90}$ – coarse A2	99	2.7	140	8.3	0.04
4	$(\text{A1})_{0.1}(\text{Si}_{0.8}\text{Ge}_{0.2})_{0.90}$ – nanosized A1	98	1.8	84	8.6	0.02

* Data points taken at 175°C

The first two samples represent baseline, bulk silicon germanium samples without additives. The first sample, A, represents an Ames Laboratory prepared doped SiGe sample while the second sample, B, represents an undoped bulk silicon germanium sample. A reduction in thermal conductivity is observed for the additive samples (1-4) if compared to the undoped, baseline sample (Sample B), however the absolute value is larger than that for the doped, baseline sample (Sample A). Note also that the percent theoretical density for the undoped, baseline sample (Sample B) was only 85%. If the percent theoretical density was closer to 100%, as exhibited by the additive samples, it is possible that the thermal conductivity would be expected to be even higher, yielding potentially a greater percent reduction in thermal conductivity. However, to validate that theory, another undoped, baseline specimen would need to be prepared and tested.

Figure 37A shows the ZT data for baseline arc melted sample compared known, bulk ZT data for silicon germanium. Figure 37B shows temperature dependent ZT values for the arc melted nanocomposite having the highest overall ZT value (Sample 3) compared to the baseline, arc melted sample (Sample B). Because the baseline, arc melted sample is undoped, its ZT values are significantly lower than bulk data. Overall, the ZT values for the additive samples are roughly equivalent to the undoped, baseline sample, indicating no significant enhancement in ZT due to the inclusion of this additive

Figure 37. (A) Temperature dependent ZT data for the baseline arc melted samples (B) Temperature dependent ZT data for the samples containing an additive phase (Sample 3) compared to the baseline HIP sample

2.7.2 Boron Carbide Nanocomposite

Preparation of bulk heterogeneous nanocomposites in the boron carbide system was considered a potential low cost alternative to layered quantum well films. ZT values reported by Hi-Z for a layered B₄C/B₉C QW material system, approximately 1.5 at 50 °C increasing to nominally 4 near 200 °C, were used as target properties. The objectives in this budget period were to 1) create dense boron carbide samples with retained nanostructure, 2) acquire the thermoelectric properties on these dense samples and vendor-supplied materials, as available and 3) compare these thermoelectric properties to bulk boron carbide and the Hi-Z reported values for QW thin films.

2.7.2.1 Processing Method Selection

The original approach envisioned fabrication of test samples by direct consolidation via hot pressing of commercial nanoparticles. Unfortunately, no commercial sources were identified, and alternate routes to synthesize boron carbide nanoparticles were evaluated. Alternate processing routes of prime interest were 1) carbothermal reduction of a nanosized boron source in the presence of nanosized carbon at high temperatures; 2) creation of nanosized boron carbide nuclei from solution by localized heating using microwave radiation; 3) controlled thermal decomposition of boron- and carbon-containing polymer precursors into phases containing nanostructured boron carbide; and 4) direct reaction between the elements obtained as nanosized materials. Carbothermal reduction is used on a commercial scale to prepare boron carbide powders, but the processing conditions necessary to create and retain nanostructure in the product are not well documented. Literature reports suggest that boron oxide and alkoxide starting materials are suitable materials for carbothermal reduction and microwave-driven reactions, but the production of significant amounts of reaction by-products and potential synthetic complexity rendered these methods unacceptable. Polymer precursors to boron carbide are reported in the literature, yet only as university research efforts, thereby limiting their availability for this program. After careful consideration, direct reaction between the elements was selected as the preferred approach based on scalability, relative simplicity, readily available materials and laboratory equipment, as well as minimized health and safety risks.

2.7.2.2. Sample Fabrication

The processing of boron carbide particles to full theoretical density is generally difficult, typically requiring temperatures in excess of 2000 °C and pressures above 3 ksi during hot pressing. Baseline samples of dense boron carbide were acquired for comparison from a commercial vendor (Ceradyne) and a research developer (Verco). These materials were used as in-house references for physical, thermal and electrical property measurements.

Initial consolidation experiments at UTRC focused on reproducing literature methods for densifying commercial powders. For preliminary densification trials, three formulations based on HC Starck HD20 B₄C (vendor reported average particle size is 500 nm as determined by laser diffraction) were prepared for subsequent hot pressing into plates nominally 1.5” wide x 3” long x 0.25” thick. Panel #1 contained B₄C plus 6 wt% carbon black as a sintering aid. The powder was dry mixed with a centrifugal high-speed mixer and hot pressed in a graphite die under argon at approximately 2000 °C and 4-6 ksi for 30 minutes.

Panel #2 contained a phenolic resin, rather than carbon black, as an alternate source of carbon. The resin produced approximately 36% carbon char by weight following thermal conversion in argon to 1000 °C. It was expected that the resin would distribute more homogeneously in the mix and aid densification of the B₄C. In this sample, the B₄C and phenolic resin (enough to yield 6% residual carbon char in the final part) were first centrifugally mixed and subsequently hot pressed under similar conditions, but with an additional intermediate hold at 1000°C to create the carbon char from the resin.

Panel #3 contained B₄C plus phenolic resin with additional boron powder in amounts designed to provide approximately 25 vol% of a target B₉C phase distributed between the B₄C initial phase, based on direct reaction between the elements. The densities of these samples, determined by vacuum infiltration of isopropyl alcohol via the Archimedes method, were 77.3%, 85.8% and 93.8% for panels #1, #2 and #3, respectively. Figure 38 below shows optical micrographs of the polished, cross-sectioned samples, as well photographs as the resulting sample plates. Sections of the densified plates were further characterized by X-ray diffraction and electron microscopy.

Figure 38. Representative hot pressed panels and corresponding optical micrographs of the polished cross – sections. (A) #1: B₄C plus carbon black, (B) #2: B₄C plus phenolic resin, (C) #3: B₄C plus B powder plus phenolic resin.

X-ray powder diffraction analysis of panels #1-#3 typically showed peaks consistent with crystalline boron carbide (one of the starting materials), while panels #1 and #2 also showed a broad peak consistent with graphite, indicative of remaining sintering aid. The diffraction pattern for panel #3 indicated peaks from the additional boron that had been intentionally added to react with residual carbon, but no residual graphitic carbon. Electron microprobe results were consistent with the X-ray data, showing generally homogeneous microstructures of boron carbide with intermixed sintering aid.

Early densification trials with only commercially available boron carbide powder and carbon powder sintering aids failed to produce sufficiently dense panels after hot pressing to 1975 °C in argon for 30 minutes. As a result, it was decided to fabricate boron carbide *in-situ* using amorphous boron metal and phenolic resin as starting materials. In order to prepare a more finely structured boron carbide material with controlled stoichiometries, three formulations targeting B₉C, B₇C and B₄C compositions (pellet samples P1, P2 and P3, respectively) were made in separate experiments using amorphous boron powder and phenolic resin. These formulations targeted the QW stoichiometries reported by Hi-Z with ZT values above 1.5. The components were separately mixed and uniaxially pressed into pellets 22 mm in diameter and heated to 1975°C in argon for 30 minutes. The retrieved pellets were sectioned for microstructural and compositional analysis, and portions were finely ground and examined by X-ray powder diffraction. Figure 39 shows the pellets before and after heat treatment. Microprobe analysis results were inconclusive and could not confirm that the targeted compositions were produced.

Figure 39. Optical photographs of uni-axially pressed pellets for target stoichiometry studies. The red lines indicate partitioning of the samples for additional X-ray powder diffraction studies and microstructural analysis of cross sections

The XRD results showed peak positions that were generally consistent with a B₄C stoichiometry in each case – suggesting that the targeted phases were not produced. XRD, however, did confirm the presence of nanocrystalline boron carbide (<200 nm by peak broadening measurement), with evidence for amorphous material in all samples and nominally 5% residual graphite in the P3 sample. As a result, this experiment provided verification that nanostructured boron carbide material was produced. Residual amorphous material and graphite are both

expected to adversely affect the electrical properties of the sample relative to ‘pure nanocrystalline’ boron carbide. Thus, further steps were needed to optimize the fabrication process.

Based on the demonstrated creation of nanostructured boron carbide from elemental starting materials with the pellets, bulk quantities of powders were prepared and hot pressed into panels using the process shown schematically in Figure 40.

For example, panel #4 was fabricated using a typical processing method as follows: a) amorphous boron powder and phenolic resin were combined and centrifugally mixed to provide nominally 25 grams each of powders targeting B_9C and B_4C products; b) each mixture formulation was created and separately heat treated in argon to $800^\circ C$ for nominally 30 minutes to convert the phenolic resin to carbon char; c) retrieved powders were separately ground, sieved to - 80 mesh (180 μm) and analyzed by X-ray powder diffraction; d) a 50:50 blend by weight of these two powders was created and centrifugally mixed to provide a homogeneously mixed powder of pretreated B_9C and B_4C ; and e) this mix was subsequently hot pressed at $1975^\circ C$ in argon for 30 minutes, and the panel designated #4 was retrieved. An additional panel, #5, was created by hot pressing a homogeneous mixture comprised of 33:33:33 HCS tarck commercial B_4C with pretreated powders of B_9C and B_4C as described above for panel #4. An additional panel #6 was fabricated from boron powder and phenolic resin to target only the B_7C stoichiometry - literature reports indicate that this phase has the highest ZT value (~ 1 at elevated temperatures of 1250K).

X-ray powder diffraction patterns were obtained on portions of samples pre-treated to $800^\circ C$ for the B_4C , B_7C and B_9C target compositions, and confirmed the presence of nanostructured material. In general, there was still an amorphous component, but this was expected considering the powders had not yet gone through the hot pressing step, where full crystallization of the powders was expected to occur. In addition, the X-ray patterns showed presence of residual elemental boron that was left unreacted at this stage.

Portions of sample panels #4-6 were cut and processed as follows: a) measured for density using the Archimedes method of liquid displacement; b) mounted and polished for optical and electron microscopy; c) ground and submitted for X-ray powder diffraction and heat capacity measurements; and d) machined to dimension for thermal expansion, Seebeck coefficient, electrical resistivity and thermal diffusivity measurements.

X-ray powder diffraction patterns were collected for the hot pressed panels #4-6. In all cases, the patterns were consistent with the presence of nanocrystalline boron carbide and confirmed that the nanostructure is retained after hot pressing the panels. Peak broadening measurements indicated that the average grain size was approximately 45 nm and 51 nm for ground portions of panels #4 and #6, respectively.

Figure 40. Schematic process for fabricating boron carbide heterogeneous nanocomposites panels via hot pressing.

While the X-ray powder diffraction patterns for boron carbide are very similar over a wide range of compositions, the actual peak positions are highly dependent on stoichiometry. The X-ray patterns for panels #4-6 were very similar, but upon close inspection, there was a measurable shift in peak positions between sample panels #4 and #6. Figure 41 shows expanded X-ray powder patterns for these samples with reference lines for B_4C and B_9C stoichiometries. Preliminary analysis shows that while the patterns were shifted, the sample targeting B_7C (panel #6, HP-7 in Figure 41) was probably closer to a B_4C formulation

Figure 41. Expanded X-ray powder patterns for portions of panels #4 (HP-5) and #6 (HP-7). Reference lines for B_9C and B_4C compositions are shown for comparison. Note the shift between patterns – boron rich stoichiometries would tend to be shifted to lower two theta values.

The physical (heat capacity, thermal expansion, density) and thermoelectric (Seebeck coefficient, thermal diffusivity, electrical resistivity) properties of boron carbide panels #4-6 were measured from room temperature to 400 °C and found to be in general agreement with bulk values for boron carbide. The calculated figure-of-merit (ZT) values at 200 °C for panels #5 and #6 were 3×10^{-3} and 5×10^{-4} , respectively, which are approximately equal to the value of bulk boron carbide, which is nominally 5×10^{-3} . While the Seebeck coefficient was increased slightly over bulk values, the density and electrical resistivity values were significantly lower than bulk values.

A 2nd generation sample, panel #7, was formulated from elemental boron and phenolic resin, but with added silicon metal (9 wt%) in an attempt to increase the electrical conductivity of the panel. This panel was hot pressed and measured to have a density of 90.4%. X-ray diffraction data on the retrieved panel indicated the presence of a mixture of B_4C , B_9C , SiC (from reaction of added Si and initial carbon) and minor amounts (totaling ~2 wt%) of SiO_2 and Mg_2SiO_4 . Subsequent analysis by X-ray fluorescence of the starting powders suggested that boron, not silicon, was a likely source of the Mg contamination. Heat capacity measurements were performed on panel #7 from room temperature to 400 °C under house nitrogen – the results ranged from about 0.9 to 1.6 J/gC in this temperature range, which are in good agreement with bulk boron carbide values.

Based on X-ray diffraction results suggesting that the targeted boron-rich boron carbide phases were not present in the hot pressed samples, elemental analysis for boron and carbon was performed by Galbraith Laboratories on several hot pressed samples and pellets targeting B_4C ,

B₇C and B₉C stoichiometries. Boron analysis was performed by ICP-OES (inductively coupled plasma-optical emission spectroscopy) and carbon analysis was performed using a standard LECO Combustion method. In all cases, results (Table 12) were consistent with a nominal B₄C composition – implying that boron was lost during the hot pressing step or that the graphite dies used for pressing had reacted with boron to produce new B₄C.

Table 12. Elemental analysis on several hot pressed panels and sample pellets

Sample	Weight % Boron	Weight % Carbon	Total Weight %	Moles C	Moles B	B/C ratio
Panel 4	78.2	20.39	98.6	7.23	1.70	4.3
Panel 5	75.3	19.33	94.6	6.97	1.61	4.3
Panel 6	66.3	19.16	85.5	6.13	1.60	3.8
Panel 7	68.5	16.80	85.3	6.34	1.40	4.5
HC Starck B ₄ C baseline	72.3	21.76	94.1	6.69	1.81	3.7
P1	69.6	21.66	91.3	6.44	1.80	3.6
P2	71.2	21.37	92.6	6.59	1.78	3.7
P3	69.1	23.08	92.2	6.39	1.92	3.3

Data based on Galbraith Lab Report data 08/30/06

The inability to fabricate a B₇C stoichiometry required development of an alternate synthetic approach. The new approach combined stoichiometric B₄C (HC Starck) with an appropriate amount of amorphous boron powder to create a boron-rich composition. In this manner, B₄C and B were combined and centrifugally mixed prior to hot pressing at 1975 °C in argon for one hour. The resulting panel, designated #8, was 96.7% dense and further sectioned for phase characterization by X-ray diffraction and thermoelectric property measurements. Figure 37 shows a portion of the resulting X-ray powder pattern along with reference lines for B₉C and B₄C stoichiometries. The experimental curve clearly lies between the two reference points and confirms the formation of a boron-rich phase. Pattern matching with simulated peak broadening provides a nominal crystal size between 65 and 94 nm – indicating that nanostructure was retained in the pressed panel.

Figure 42. Expanded X-ray powder patterns for panel #8 (HP-9). Reference lines for B₉C and B₄C compositions are shown for comparison. Note the shift between patterns, indicative of a boron rich composition.

The critical thermoelectric properties for panel #8 (HP-9), and comparative data for boron carbide bulk materials and the other hot pressed panels at nominally 200 °C are shown in Table 13.

Table 13. Summary of thermoelectric properties acquired during BP2 for the boron carbide system (taken at 200 °C)

Sample	Description	% Theor. Density	Heat Capacity (J/g °C)	CTE, α (ppm/°C)	Electrical Resistivity, r (mohm-cm)	Seebeck Coefficient S (mV/K)	Thermal Conductivity k (W/m-K)	ZT
A	QW Film (Hi-Z)	-	-	-	0.4	1046	(12)	~3.2
B	Bulk Boron Carbide	100	1.5-1.8	5.3	~80 (b)	~270 (a) ~120 (b)	~23 (b)	~0.0006 (b) ~0.0015 (c)
C	Vercor Boron Carbide	99	1.69	-	140	340	(23)	~0.001
D	Ceradyne Boron Carbide	100	(1.70)	-	100	270	(17.2)	0.002
HP-5	B plus phenolic resin to give mixture of B4C/B9C	83	1.54	5.5	364	327	14.3	0.001
HP-6	Commercial B4C mixed with pretreated B plus phenolic resin	90	1.55	5.5	167	315	11.0	0.003
HP-7	B plus phenolic resin targeting B7C	81	1.75	5.8	860	385	17.2	0.0005
HP-8	B plus phenolic resin targeting B7C plus 9 wt% Si	91	1.34	6.8	433	335	15.6	0.0009
HP-9	Reaction of B4C plus B	97	1.45	5.3	80	256	9.9	0.0039

(a) Aselage and Emin, DOE High Efficiency TE Review, March 2002

(b) Bouchacourt and Thevenot, *J. Mat. Sci.* **20** (1985) 1237-1247

(c) Aselage, *Mat. Res. Soc. Symp. Proc.* **234** (1991) 146-156

In summary, key accomplishments during this budget period for the fabrication tasks of boron carbide heterogeneous nanocomposites include:

1. Developed method to fabricate high density, nanostructured boron carbide panels via low temperature mixing and hot pressing near 2000 °C in argon
2. Demonstrated use of phenolic resin as a source of carbon char for direct reaction with boron to form boron carbide
3. Demonstrated fabrication of a panel with a boron-rich, boron carbide stoichiometry

4. Measured thermoelectric properties on nanostructured panels that are essentially equivalent to bulk boron carbide at temperatures below 400 °C.
5. Obtained calculated ZT values for the nanostructured boron carbide which range from 0.0005 to 0.0039 at 200 C, and which are significantly less than the value of about 4 for layered QW materials reported by Hi-Z, but equivalent to bulk boron carbide values.

3.0 Budget Period 3 Plan

After the Budget Period 2 review on October 10th, 2006, the DOE elected not to continue with this program.

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