QUANTUM WELLS THERMOELECTRIC DEVICES FOR DIESEL ENGINES

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BACKGROUND

Thermoelectric materials are utilized for power generation in remote locations, on spacecraft used for interplanetary exploration, and in places where waste heat can be recovered. Broader usage is limited by the efficiency of present systems and the power-specific cost ($/W) of power generation. Materials with a $ZT \geq 6$ can lead to a factor of 2 to 3 improvement in thermodynamic efficiency. Recall that the thermodynamic efficiency, η, of a thermoelectric power generator is

$$\eta = \frac{T_h - T_c}{T_h}\left[\frac{M - 1}{M + T_c/T_h}\right] \qquad (1)$$

where M is defined as

$$M = \sqrt{1 + \frac{1}{2}\bar{Z}\,(T_c + T_h)} \qquad (2)$$

and T_h is the absolute temperature at the hot junction and T_c is the absolute temperature at the cold junction. To achieve a high efficiency with a power generator, the overall figure of merit for the device, Z, must be high. The figures of merit of the thermo-electric materials used to construct the device must also be high. For a specific material, Z is defined as:

$$Z = \frac{\sigma\alpha^2}{\kappa_{ph} + \kappa_{el}} \qquad (3)$$

where σ is the electrical conductivity, α is the Seebeck coefficient, κ_{ph} is the phonon contribution to the thermal conductivity, and κ_{el} is the electronic contribution to the thermal conductivity. Note that κ_{ph} is also known as κ_L, the lattice thermal conductivity. Much of the effort to improve Z over the past 20-30 years has focused on attempts to reduce κ_L without adversely affecting the electrical conductivity. Some success has been achieved with solid-solution alloying. Further reductions in κ_L have been achieved by reducing the grain size of silicon-germanium alloys, however, this approach is still in its infancy and the potential benefit is believed to be relatively small.

Multilayer films of B_4C/B_9C and $Si/Si_{0.8}Ge_{0.2}$ are being investigated as a means of achieving a high Z. Models based upon quantum mechanics predict that such structures should have an unusually high Z [1-5]. The quantum-well (QW) layer is sandwiched between two barrier layers. Typically, the QW material has a very narrow band gap and the barrier material has a relatively large band gap. Molecular beam epitaxy (MBE) and sputtering have been employed to fabricate the samples.

For power applications, the concern is that the above materials will inter-diffuse at some elevated temperature and lose their two-dimension structure and associated quantum well properties. For power generation applications, B-C and SiGe alloys appeared to be the best initial selection for the following reasons:

- B-C have very low diffusion coefficients in one another.
- Si and Ge have very low diffusion coefficients in one another. The dopants boron and phosphorous however can diffuse much quicker and high temperature aging studies will be necessary to determine how long these films will remain stable at the anticipated operating temperatures.

- B-C as well as SiGe alloys do not have to be deposited in an exact stoichiometry to be useful thermoelectric materials.
- Since stoichiometry is not critical, the deposition process can be conducted with less critical controls.

EXPERIMENTAL

α and ρ Measurements

Room temperature resistivities were measured on samples using the following method: the current was introduced at the ends of a long, rectangular cut sample and the voltage probes were near the center of the test specimen. The resistance was obtained from the voltage drop, and the resistivity was calculated by knowing the cross-sectional area of the bar and the distance between the two voltage probes (ASTM F-43). The Allesi instrument, which uses pressure contacts, was used as the voltage probes in this case.

The high temperature α and ρ of the films were measured in a system at Hi-Z and the results have been published previously [4, 5]. The electrical resistivities of the sam-ples were measured as a function of tem-perature from 300K to 1200K using a Linear Research LR400 4-wire bridge operating at 16Hz. Electrical contact to the films was made by wrapping nickel wire around the sample, and bonding the wires to the surface with silver paint. The thermocouple leads were held to the surface of the sample with the nickel wires, and bonded in place with the silver paint. Currents for the measurements were in the range of 1 to 100 mA.

QW Device

A B_4C/B_9C-Si/SiGe P-N device (shown in Figure 1) with low contact resistance was fabricated and the results appear very promising. Each leg in this couple consists of a square of 1000Å thick multilayer of B_4C/-B_9C (P type) and Si/SiGe (N type) films. The films are deposited on 0.5 mm thick silicon substrate that is approximately 1cm×1cm. At a $\Delta T \approx 50°C$ ($T_{cold} \approx 40°C$ and $T_{hot} \approx 90°C$), the voltage measured on this couple was ~ 0.1 Volts. The contact resistance was a few ohms which was very low compared to the total resistance of the couple which was approximately 20 kΩ. This is the resistance of the films and does not include the Si substrate [4, 5]. The results are tabulated in the Table 1. (Efficiency was obtained as follows: {i} Power data, α and ρ, were measured at a T_{hot} = 90°C and T_{cold} = 40°C. {ii} The Z for the couple, over the ΔT = 90°C - 40°C, was calculated using bulk thermal κ property data. {iii} Efficiency was then calculated using the formulas 1 through 3.

These values of voltage and resistance give a matched load power of about 0.125 μW (micro-Watts) for the couple at a $T_{cold} \approx 40°C$ and $T_{hot} \approx 90°C$. At these same temperatures and dimensions a bulk Bi_2Te_3 couple produces only 0.01 μW, a bulk B_9C-SiGe couple produces only 0.004 μW, and a bulk

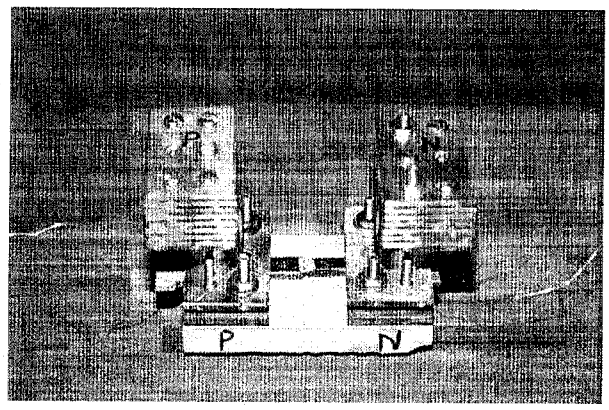

Figure 1. Schematic of P-N couple test fixture.

SiGe couple produces 0.02 μW. Therefore the B_4C/B_9C-Si/SiGe P-N couple produces about ten times more power, than the bulk BiTe couple and about thirty times more power than bulk B_9C-SiGe couple. Although this couple was fabricated with thin films (only 1000Å), Hi-Z hopes to duplicate these results with much thicker films (100,000Å) on a thinner or insulating substrate. Silicon substrates with thicknesses of 5μm (micro-meter) and 10μm are available commercially as are insulating substrates like Kapton. If fabrication of thick films on these substrates is successful then a 1cm×1cm couple, like the one described above, would produce 1250μW of power at a $\Delta T \approx 50°C$. The final goal is to fabricate and measure the properties of these thicker P-N couples on

very thin or insulating substrates. These results are summarized in Table 1.

Table 1	Voltage & Resistance Measured Power (μW) EXPERIMENTAL	Calculated Efficiency (%) $T_{cold} \approx 40°C$ and $T_{hot} \approx 90°C$ THEORETICAL
B_4C/B_9C-Si/SiGe P-N couple	**0.125**	**4**
Bulk Bi_2Te_3 Couple	0.01*	3
Bulk SiGe Couple	0.02*	<1
Bulk B_9C-SiGe Couple	0.004*	<1

THERMOELECTRIC FOR DIESEL ENGINES

The auxiliary power requirements for heavy-duty trucks continues to increase. This will be particularly true when the power required to operate systems to reduce NO_x and particulates are introduced. If something is not done to reduce the engine auxiliary power load, these cleanup systems could essentially double the auxiliary power requirements which will result in a significant increase fuel consumption.

Hi-Z has been working for several years to develop a system that can reuse the waste energy available in the engine's exhaust to provide the auxiliary power for the truck [11]. The system we are currently testing on a class 8 truck in place of the muffler. This generator uses thermoelectric modules made of bismuth-telluride to convert the exhaust heat directly to 1kW of electricity with an efficiency of about 5%. A study of replacing the alternator with a 1kW thermoelectric generator completed in 1992 [12] showed that while the projected cost at the 1kW thermoelectric generator is more than a comparable alternator, the break even time for a Class 8 truck using such a system should be about two years in the United States and about eight months overseas.

This study only considered replacing the alternator. However, there are gains in fuel economy to be made if some of the other engine driven auxiliaries can be replaced by electric driven components whose power is derived from waste heat rather than from the engine shaft. These auxiliary devices could include the fan, power steering, power brakes, air compressor, NO_x and particulate cleanup systems, and possibly air conditioning.

Figure 2 is an energy diagram for a typical LE55 Diesel engine. This figure also shows the same engine with a 5% efficient thermoelectric generator. One sees that the efficiency of the engine is increased almost two percentage points using the thermoelectric generator.

One has two choices to reduce the break-even times. The first is to reduce the cost of the generator components and the second is to increase the system conversion efficiency.

Reducing component cost is difficult to do by itself. It can be more easily achieved, however, when the conversion efficiency is increased because one needs to transfer and convert less energy to provide the same output power. This results in fewer, smaller, and, therefore, cheaper components being required which should result in a lower cost and, therefore, a shorter break-even time.

Hi-Z is approaching the problem of increasing system efficiency in two ways. The first is a near term program which should bear fruit within the next few months and the second is a long term program which may require several years to complete.

Hi-Z has been developing multilayer quantum well (MLQW) thermoelectrics for several

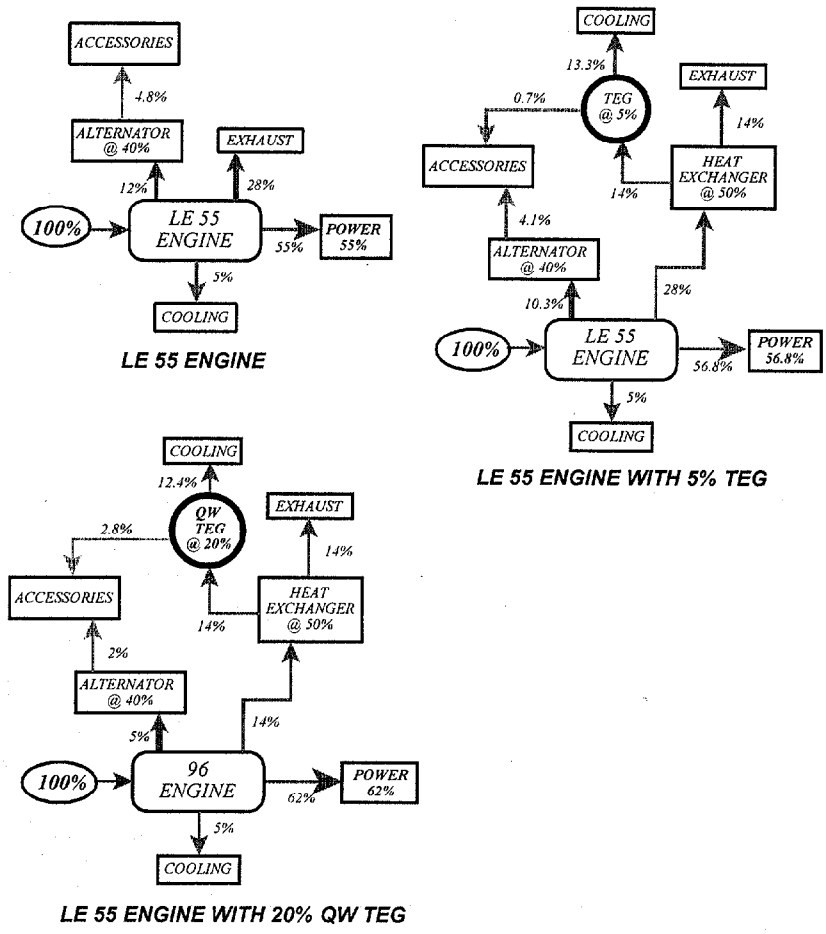

Figure 2. Energy Diagram of LE 55 Engine

years. These materials consist of very thin (100Å) alternating layers of materials with two different electron band gaps. When prop-erly fabricated, the resulting material has very much improved thermoelectric proper-ties compared to the same basic material made by conventional bulk methods.

Two types of MLQW systems have been discovered to date and both are now being developed under contracts to DOE. These systems are the silicon-germanium MLQW [14] and the boron carbon MLQW [15]. The

silicon-germanium MLQW data indicate they will be used for cooling applications while boron carbon MLQW indicate they are good for power production. The boron carbon MLQW will be discussed first.

One of the problems that remain to be solved with the boron-carbon MLQW is that it can only be made as a P-type material. We are currently investigating other materials system to see if we can develop an N-type MLQW material with high temperature capability sim-ilar to that of the boron-carbon MLQW.

A conventional N-type bulk alloy such as bis-muth-telluride can be used with the P-type boron-carbon MLQW materials to form the required couples. This will not result in con-version efficiencies as high as a system which uses both N– and P-type MLQW, however, the theoretical conversion efficiencies are still significantly higher than that provided by a system which uses only conventional bulk alloys. The current esti-mate is that a thermoelectric conversion sys-tem which uses a boron-carbon MLQW for the P legs and conventional bismuth-telluride for the N leg will have a conversion efficiency

of about 20%.

Figure 2 shows the energy balance for a conventional LE 55 engine. Since there is less energy content in the exhaust of the LE 55 than the present day (96) engine, less energy is available for conversion. However, the inclusion of a thermoelectric generator with 20% efficiency would still improve the efficiency of the LE 55 by over 7 percentage points or 12.7%, as shown in Figure 2.

It appears possible that the conversion efficiency of a MLQW device could be as high as 40% if a high temperature N-type materials can be identified. If that does happen, then the energy balance for the LE 55 with an advanced thermoelectric generator could be as shown in Figure 2. This energy balance shows a potential efficiency improvement of almost 10 percentage points or 18% over the LE 55's nominal 55 percent efficiency.

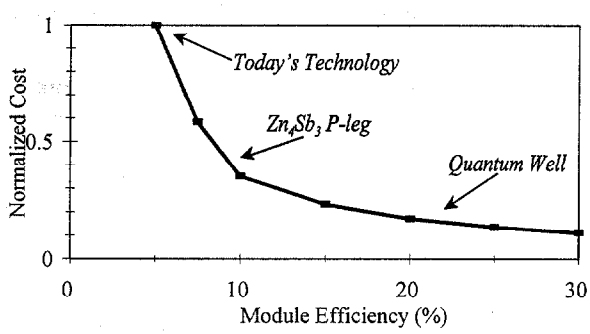

Figure 3. Normalized module cost versus conversion efficiency for small generator.

CONCLUSION

The overall engine efficiency of large Diesel engines can be improved by adding a thermoelectric generator to convert some of the energy available in the exhaust to useful electric energy. The overall percentage improvements which can be expected from current materials is low. However, new materials are being developed which can lead to significant improvements in overall engine efficiency over the next several years. Some of these materials will be available within a few months while more advanced materials will require several years of devel-opment. Incorporation of these new ther-moelectric materials should lead to a sig-nificant improvement in overall engine effici-ency as well as a shorter break-even time. While the improvements expected are greater when thermoelectrics are applied to present day engines, it will also significantly improve the efficiency of the advanced LE 55 engine.

Cost of Quantum Well Module

Cost of a generator with 30% conversion efficiency modules will be about 10% of a generator with 5% conversion efficiency modules as it is shown in Figure 3. Conversely, for generators of the same size, the power output of a generator with 30% conversion efficiency modules will be about 10 times that of a generator with 5% conversion efficiency modules.

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