SCALE UP OF Si/Si$_{0.8}$Ge$_{0.2}$ AND B$_4$C/B$_9$C SUPERLATTICES FOR HARVESTING OF WASTE HEAT IN DIESEL ENGINES

Peter M. Martin
Pacific Northwest National Laboratory

Larry C. Olsen
Pacific Northwest National Laboratory

ABSTRACT
Thermoelectric devices show significant promise for harvesting and recovery of waste heat from diesel engines, exhaust systems and industrial heat sources. While these devices convert a heat flow directly into electrical energy, cooling can be accomplished by the same device with application of a direct current (Peltier effect). Conversion efficiencies of bulk thermoelectric systems, however, are still too low for economical power conversion in diesel powered vehicles and heavy vehicles. Thermoelectric superlattice devices have demonstrated the potential for increased efficiencies and utilization of waste heat. Although reported efficiencies are well above 15%, fabrication costs are still too high for use in diesel engine systems. To realize this efficiency goal of ~ 20% and power generation in the kW-MW range, large quantities of superlattice materials are required. Additionally, if the figure of merit (ZT) of these superlattices can be increased to > 2, even less superlattice material will be required to generate electric power from heat in diesel engines. We report on development of and recent progress in scale up of Si/ Si$_{0.8}$Ge$_{0.2}$ and B$_4$C/B$_9$C superlattices for thermoelectric applications, and particularly for fabrication of large quantities of these materials. We have scaled up the magnetron sputtering process to produce large quantities of Si/ Si$_{0.8}$Ge$_{0.2}$ and B$_4$C/B$_9$C superlattices with high ZT at low cost. Quantum well films with up to 1000 layers were deposited onto substrate areas as large as 0.5 m$^2$ by magnetron sputtering. Initial studies showed that the power factor of these SL’s was high enough to produce a ZT significantly greater than 1. Both p- and n-type superlattices were fabricated to form a complete thermoelectric power generating device. ZT measurements will be reported, and based on measured power factor of these materials, should be significantly greater than 1. These results are encouraging for the use of quantum well materials in thermoelectric power generation.

INTRODUCTION
Thermoelectric devices show significant promise for harvesting and recovery of waste heat from diesel engines, exhaust systems and industrial heat sources. Just a sample of existing heat sources includes exhaust gases from vehicles (particularly heavy vehicles), fuel cells, gas turbines, industrial processes, and reactor systems. Preliminary work has already been accomplished for implementing thermoelectric devices in exhaust systems of diesel engines [1]. Conversely, thermoelectric cooling (Peltier effect) can be used to remove heat from electrical devices and for refrigeration. Conversion efficiencies of bulk thermoelectric systems, however, are still too low for economical power conversion in diesel powered vehicles and heavy vehicles.

A measure of the power conversion effectiveness of a thermoelectric material is the figure of merit $ZT = (S^2σ/κ)T$, where $S$ is the Seebeck coefficient, $σ$ is the electrical conductivity and $T$ is the absolute temperature. Thermoelectric modules consist of a p-type leg and n-type leg as shown in Figure 1. A temperature difference across the p-n couple causes heat and charge carriers to flow (Seebeck effect) and power is generated when connected to an external circuit. The efficiency of such a system depends on the electrical and thermal conductivity, and the Seebeck coefficient of the material/structure [2].

In the last decade, new materials and structures with increased values of the material figure of merit, ZT, have been developed for thermoelectric energy conversion and cooling. Whereas the ZT values for thermoelectric materials were apparently pegged at 1.0 from 1970 to 1990, values greater than 2.0 were reported in the 1990s [3]. The increased values for ZT indicate that efficiencies greater than 20 % and coefficient of performance values greater than 2 are possible for power production and refrigeration, respectively. Low dimensional structures show promise for improved thermoelectric performance and power conversion efficiencies. Some of the most encouraging results have been achieved for thin film superlattice and quantum well structures [4,5,6]. Virtually all structures to date have been deposited by molecular beam epitaxy (MBE) and magnetron sputtering on a
small scale. In additional to the technical challenges, two major factors that are critical to a functional device have yet to be demonstrated. The first is the need for a cost effective deposition process; the deposition process currently being used is too slow, costly and unscaleable. Quantum well structures may have thicknesses up to 100 µm. Use of MBE to deposit these structures would be exceedingly cumbersome and lengthy. The other major factor holding up this technology, however, is the demonstration of scaled-up quantum well devices with performance comparable to those reported for small scale. Current devices have a surface area of only ~ 1 cm². To meet current power and cost requirements, large area devices would be required [5]. Accordingly, we are evaluating the magnetron sputtering process for fabrication of large area thermoelectric quantum well structures.

**Figure 1.** Typical p-n thermoelectric power generating/cooling module.

**Figure 2.** Theoretical efficiency versus figure of merit ZT.

We report on development of and recent progress in scale up of B$_2$C/B$_4$C and Si/SiGe quantum wells for thermoelectric applications. The bulk of the previous work on this structure was performed using MBE with only a small number of magnetron sputtering efforts reported [6]. All quantum well structures were deposited on single crystal substrates, and only on a small scale. Crystalline material, which it is thought to be necessary for good thermoelectric properties, can be deposited using MBE. However, we will report that comparable, and possibly improved properties, can be obtained with magnetron sputtering.

**QUANTUM-WELL DEPOSITION AND PROCESS SCALE-UP**

MBE and magnetron sputtering processes are used to deposit Si/Si$_{0.8}$Ge$_{0.2}$ quantum well structures and magnetron sputtering is primarily used to deposit B$_2$C/B$_4$C structures. PECVD is also used to deposit BC thin films [7]. As stated above, these structures are deposited only on a small scale, with little evaluation of how deposition conditions affect the thermoelectric and electric properties. While the MBE process provides single crystalline structures (which may or may not be the most desirable), deposition rates are low and scale up to large area substrates is expensive and cumbersome. The work described here using magnetron sputtering took place in two phases: (1) demonstration and replication of quantum well films on a small scale and (2) quantum well film process scale up. The objective of Phase 1 was to establish a baseline for the scaled up process in Phase 2 and to compare thermoelectric properties with results reported by others [4,6,8,9].

In Phase 1 Si/Si$_{0.8}$Ge$_{0.2}$ and B$_2$C/B$_4$C quantum well films were deposited onto 1" single crystal Si substrates in a small box coater, described in another paper [10]. A rotating substrate holder was placed 15 cm above the Si and Si$_{0.8}$Ge$_{0.2}$ or B$_2$C and B$_4$C sputtering targets. While the substrate could be heated to temperatures as high as 800 °C, depositions were performed at ambient (88 °C), 200 °C, 300 °C, 400 °C, and 600 °C for the Si and SiGe films, and 88 °C and 500 °C for BC films. Substrate temperature was measured by thermocouples placed at each substrate position. Diameter was 15.2 cm. RF power densities applied to the sputtering targets ranged from 1.1 W/cm$^2$ to 3.3 W/cm$^2$. All depositions used high purity Ar as the sputtering gas. Deposition rates depended on power applied to the sputtering target, substrate target separation, gas pressure and substrate temperature, and ranged from 1 Å/s to 6 Å/s for Si and SiGe films and ~ 0.13 Å/s for BC films.

Quantum well depositions were performed by moving the substrate sequentially from over the one target (Si or B$_2$C) and then over the other (Si$_{0.8}$Ge$_{0.2}$ or B$_4$C) target. Before deposition, the substrate was heated to the required temperature by a resistive heater. The first layer deposited was the high band gap material (Si or B$_2$C) layer. Each layer was ~100 Å thick. Thickness was determined simply by time of deposition. For initial evaluations, 100 – 300 –layer quantum well structures were deposited onto single crystal Si substrates. The electrical conductivity of the quantum well structures and single layer films was measured by the four point van der Pauw technique and the Seebeck coefficient (thermopower) was measured by applying a temperature gradient across the sample and measuring the voltage across the sample. All measurements were in-plane. The Seebeck coefficient and conductivity of the substrate were measure before and after deposition. The Seebeck coefficient and conductivity of the film were calculated using standard techniques [6].

In Phase 2, the deposition process was scaled up to deposit quantum well structures on twelve 10 cm Si wafers or substrate areas of 0.5 m². Figure 3 shows a picture of the modified substrate holder and heater assembly. The following chamber modifications were made to scale up the deposition process:

- Four quartz heaters were placed above the substrate holder to achieve uniform heating over an area of 0.5 m².
- Shields were placed between the sputtering cathodes to prevent cross talk
- A precision stepper motor was attached to the substrate rotation assembly for precise thickness control
- Both sputtering cathodes were in continuous operation.
In this configuration, the substrate holder rotated continuously over the sputtering targets with the rotation rate and deposition rate tuned for each target to obtain a layer thickness of 100 Å. This deposition geometry posed several concerns. The major concern was that the crystal orientation and the resulting thermoelectric properties would degrade due to the increased angles of incidence of the sputtered atoms and associated shadowing. Other concerns were the extent of cross talk between cathodes, uniformity of coverage and the overall robustness of the system with thermal cycling.

Figure 3. Scaled up heater and substrate holder assembly.

RESULTS AND DISCUSSION

Single layer Si and Si_{0.8}Ge_{0.2} films and Si /Si_{0.8}Ge_{0.2} quantum well structures with the highest electrical conductivity, highest Seebeck coefficient and largest value of power factor (S^2) were deposited at a substrate temperature of 400 °C. Single layer B,C and B,C films had highest electrical conductivity and Seebeck coefficient when deposited at 500 °C. B,C/B,C quantum well structures have yet to be evaluated in detail. Figure 4 summarizes performance results for small scale depositions, by plotting measured absolute Seebeck coefficient against conductivity. Also shown in the figure are asymptotic curves for a range of power factor values, where this quantity is given by S^2T. Typical values of S were ~ 800 µV/K, s between 100 and 1000 (O.cm)^{-1} and power factors between 0.01 and 0.20. The values shown in Figure 3 are comparable or better than those previously reported for MBE-deposited and sputter-deposited quantum wells [6,8,9]. We were able to deposit both n-type, and for the first time reported in the literature, p-type Si /Si_{0.8}Ge_{0.2} quantum well structures. In contrast to the literature, it was also possible to deposit n-type B,C and B,C films. Direct measurements, however, of ZT needed to complete the evaluation of thermoelectric properties require a lift off of the quantum wells and are in progress.

It is difficult to speculate on the reasons for the improved thermoelectric properties of the magnetron-sputtered quantum wells. It was important, however, to preserve the electric properties (carrier concentration, mobility) while minimizing the thermal conductivity of the quantum wells. The improvements might be due to enhanced acoustic phonon scattering at interfaces and grain boundaries [11,12].

Figure 4. Thermoelectric properties of Phase 1 single layer films and Si/Si_{0.8}Ge_{0.2} quantum wells structures.

Figure 5 summarizes the thermoelectric properties of all single layer films and quantum wells, including scaled up depositions. Both Figures 3 and 4 demonstrate the effects of quantum confinement as predicted by Hicks and Dresselhaus [5]; i.e., the power factors of quantum well structures are significantly higher than those of single layer films. Note that the power factor of single layer B,C and B,C films are in the range of the Si /Si_{0.8}Ge_{0.2} quantum wells. Thus, with quantum confinement effects, B,C/B,C quantum well structures should have power factors significantly higher than those of the single layer films. Thermoelectric properties (Seebeck coefficient) of single layer films and the quantum wells were essentially the same as those of the small scale films, but the conductivity was as much as an order of magnitude less than the best films. This decrease in conductivity might have been due to increased impurities in the films. While the deposition rates were the same as small scale films, the heating of a 0.5 m² substrate also heated the sides of the deposition chamber. As a result, gases evolved from the chamber walls and shielding that could have degraded electrical properties. A pre-deposition bake out at 400 °C and an over night pump down were required to eliminate contaminants in the chamber. The reduced conductivity also reduced the power factor, which might be the price to pay for large area deposition. However, with the fully-automated scaled up process, there was virtually no limit on the number of layers that can be deposited.

Figure 5. Thermoelectric properties of small scale and scaled up B,C/B,C and Si/Si_{0.8}Ge_{0.2} single layer films and quantum well structures.

SUMMARY

Devices utilizing Si /Si_{0.8}Ge_{0.2} and B,C/B,C quantum wells structures have the potential to provide efficient thermoelectric power generation. Scale up of the deposition process is one of the factors that must be achieved before thermoelectric devices can provide power at a reasonable cost. A scaled up magnetron sputtering process for quantum wells deposition was demonstrated, and n-type, and for the first time, p-type quantum wells were deposited. Typical Seebeck coefficients were near 800 µV/K, conductivities between 100 (O.cm)^{-1} and 1000 (O.cm)^{-1}, and power factors near 0.025 (300K) were.
achieved. The typical deposition time for a 100-layer quantum wells was 100 m. Test structures have between 100 and 300 layers, but with the scaled up process, there is virtually no limit on the number of layers that can be deposited.

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