Si/SiGe Quantum Well Thermoelectric Materials and Devices for Waste Heat Recovery From Vehicles and Industrial Plants

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Abstract

Fabrication development of high efficiency quantum well (QW) thermoelectric continues with the P-type and N-type $Si/Si_{80}Ge_{20}$ films with encouraging results. These films are fabricated on Si substrates and are being developed for low as well as high temperature operation.

Both isothermal and gradient life testing are underway. One couple has achieved over 4000 hours at T_H of 300°C and T_C of 50°C with little or no degradation. Emphasis is now shifting towards couple and module design and fabrication, especially low resistance joining between N and P legs. These modules can be used in future energy conversion systems as well as for air conditioning.

Introduction

Hi-Z Technology, Inc. (Hi-Z) is currently developing many different thermoelectric generator designs that are used to convert waste heat or heat sources directly to electricity. These include waste heat recovery from diesel trucks as well as automobiles and thermoelectric power generators including space application.

Bi_2Te_3 alloys, PbTe alloys, and SiGe based materials are presently used for power generation in remote locations, for example in deep space probes or direct conversion in general. However in most waste heat recovery and direct heat conversion applications an improvement in the efficiency of the energy conversion process from heat into electricity is needed. The efficiency of thermoelectric energy conversion devices is strongly limited by the performance of the materials, which is normally measured in terms of a *Figure of Merit* Z (see next section).

The breakthrough approach to increasing Z is to form compositionally modulated materials, mainly by QW confinement of carriers in the active layers in a multilayer film by adjacent barrier layers. The core concept is to enclose each electrically active layer by a material which has a band offset sufficient to form a barrier for the charge carriers. The major improvement in Z is expected to follow from an increased Seebeck coefficient that results from an increase in the density of states. There may also be a significant increase on the carrier mobility due to quantum confinement, so ideally there is an improvement in Z from the Seebeck coefficient, and the electrical conductivity. Also, the thermal conductivity, is reduced due to strain between the QW and barrier layers which in turn inhibits phonon flow. The next section shows the detailed explanation. QW effects become significant only when the thickness of the active layer is small, i.e., below about 200Å. The effectiveness of QW confinement and its effect on the figure of merit depends on many factors such as the carrier concentration, which is temperature dependent.

In addition to QW confinement, improvement in Z may result from the periodicity of the multiple film structure on the thermal conductivity *[1]*. At low values of the thickness of individual layers, there may be interference with the propagation of phonon modes, and therefore a reduction in κ_L. The theory of this effect, and its application to both in-plane and cross-plane thermal conductivity values, is now a subject of intense research and may evolve into a field of engineered thermal transport independently of thermoelectricity *[2&3]*.

Nomenclature

A	amperes	α	Seebeck coefficient
Å	angstroms	κ	thermal conductivity
k	kilo (10^{+3})	ρ	resistivity
m	milli (10^{-3})	Ω	ohms
M	matching factor	μ	micro (10^{-6})
T_C	cold side temperature	W	watts
T_H	hot side temperature	V	volts
T	mean temperature	Z	figure of merit

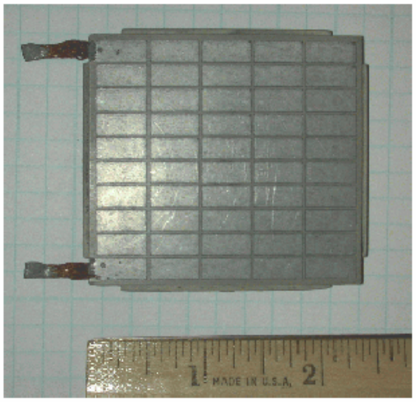

Figure 1. Hi-Z Thermoelectric Module

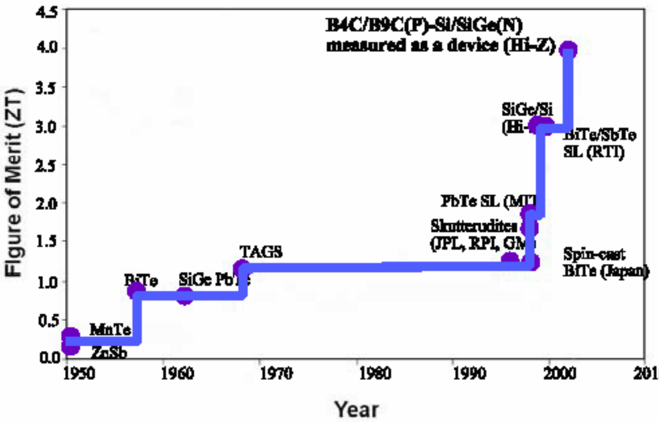

Figure 2. ZT Time Line.

Recent Advances

Hi-Z currently uses conventional Bi_2Te_3 alloy thermoelectric modules, as shown in Figure 1 *[4]*. The material in these modules has a value of ZT (figure of merit Z, times its mean absolute operation temperature T) of about 1. As shown in Figure 2, the value of ZT has hovered around 1 since the mid-1950s when semi-conductor materials were introduced into thermoelectric conversion. In the late 1990s new materials, including quantum well materials, were developed and a value of 4 has been achieved with B_4C/B_9C and with some promise that even higher values can be obtained as development continues.

The figure of merit (Z) for a thermoelectric material is obtained from its electric and thermal properties by

$$Z = \alpha^2 / (\rho \cdot \kappa)$$

where α is the Seebeck coefficient of the material, V/K, ρ is its resistivity, ohm-cm, and κ is its thermal conductivity, W/cm K. Efforts to improve the value of Z for a bulk material often fails because as one increases α, the values of ρ and/or κ usually also increase so that the resulting value of Z either remains the same or decreases.

Table 1 shows the measured thermoelectric property of Hi-Z QW samples, while Figure 3 shows the measurements setup. For this recent low resistivity QW thermoelectric sample, also measured by UCSD, and observed by NIST using the Hi-Z facility. Two measurements for electrical resistivity are shown: the two probe technique that includes the InGa electrical contacts and QW film while the second approach, the 4 probe technique allows the film resistivity to be measured because it is independent of contact resistance. It is not obvious why this specimen is exhibiting such a low 4 probe resistivity value although special efforts were made to improve the wetting of the liquid metal InGa contacts. Additional samples are being prepared to determine if the results can be obtained on multiple samples. NIST will further confirm the measurements using their measurement systems in the future.

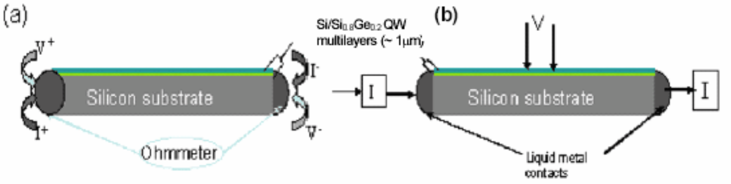

Figure 3. Schematic of the Measurement Setups for Obtaining the Resistance (ρ) of the Si/SiGe Multilayers on Si substrates using: (a) two-terminal Ohmmeter (Tegam Inc.) Probes, an (b) a four probe arrangement, where the current is sent through the liquid metal contacts at the ends while the voltage is measured along the sample with two more probes. Note: Typical design is grown to 8-10 μm of Si/SiGe multilayers. Test specimen had 1 μm Si/SiGe multilayers.

Hi-Z has performed thermal conductivity measurements of QW films in the past using the most reliable technique, the 3-ω method, and these measurements support the large reductions in the κ of these thin films. Such measurements are very difficult to conduct and further thermal measurements such as efficiency and κ are planned with these low resistivity films. When additional data become available, Hi-Z will start using the lower QW thermal conductivity value in the analysis. Table 1 also shows typical Bi_2Te_3 data for comparison.

Si/SiGe QW Thermoelectric

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

$$\eta = \frac{M-1}{M+\frac{T_c}{T_h}} \times \left(1-\frac{T_c}{T_h}\right) = \frac{M-1}{M+\frac{T_c}{T_h}} \times \eta_{Carnot} \tag{1}$$

where M is defined by

$$M = [1+Z(T_c+T_h)/2]^{½} \tag{2}$$

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

For a specific material,

$$Z = \sigma\alpha^2/(\kappa_L + \kappa_e) \tag{3}$$

where σ is the electrical conductivity, α is the Seebeck coefficient, κ_L is the lattice or phonon contribution to the thermal conductivity and κ_e is the electron contribution to the thermal conductivity. Note that the term to the right of Equation 1, is Carnot efficiency, which only has values between zero and one, so the "η" is always a fractional multiplier of Carnot efficiency.

The breakthrough approach to increasing Z is to form compositionally modulated materials (*e.g.*, Si/SiGe), mainly by QW confinement of carriers (electrons and holes) in the active layers (SiGe) in a multilayer film by adjacent barrier layers (Si). The core concept is to enclose each electrically active layer by a material which has a band offset sufficient to form a barrier for the charge carriers. The major improvement in Z is expected to follow

Table 1. Performance of P-type Si/SiGe QW films. Recent Hi-Z Seebeck coefficient and electrical resistivity data, confirmed by UCSD and observed by NIST using Hi-Z facility. Bi_2Te_3 bulk alloy data is shown for comparison.

	Measured Seebeck Coefficient α, **μV/K**	**Measured Electrical Resistivity** ρ, **mΩ-cm**	**Power Factor** α^2/ρ **μW/cm°K²**
Typical former QW sample at room temperature	1100	1.0	1,210
Recent QW sample material Measurements confirmed by UCSD and NIST	1200 1200	0.8 (2 probe technique) 0.04 (4 probe technique)	1,800 36,000
Bi_2Te_3 Bulk Alloy	220	1.1	44

from an increased Seebeck coefficient that results from an increase in the density of states from bulk (3D) to two dimensional (2D) quantum confinement. There is also a significant effect on the electrical and thermal conductivities due to quantum confinement, so ideally there would be improvement in Z from the α, σ, and κ terms of equation 3. QW effects become significant only when the thickness of the active layer is small, below about ~200Å. In simple terms, QW effects are caused by quantum confinement which means, the carriers (electrons and holes) are confined in two dimensions as compared to the bulk material where the carriers are moving in three dimensions. The reduction in the dimensions of movement reduces the scattering centers of the carries, therefore the mobility is increased which makes the electrical conductivity (σ) increases. We have measured the mobility of the samples which show this enhancement. That increases the Z, which in turns increases the efficiency. The confinement reduces the thermal κ, since the wavelength of the phonons are larger than the electrons and holes. It has been shown experimentally and theoretically ~1/3 reduction in thermal κ *[5]* of QW compared to bulk. It is this confinement in the QW (the two dimensionality) that increases the Z and then the η.

The temperature dependent Seebeck coefficient is a function of the Fermi level and provides the basic information about the band structure and the density of states at the Quantum Well (QW) layers. From this information the observed Seebeck coefficients can be developed as described below. Additionally, information is provided about the various carrier scattering mechanisms.

The standard form of the electron dispersion in a QW layer is free electron like parallel to the layers, and tight binding like perpendicular to the layer.

$$E(k_{\parallel}, k_{\perp}) = \frac{\hbar^2 k_{\parallel}^2}{2m_*} + t(1 - \cos k_{\perp} d)$$

where m_* is the conduction band effective mass, t is the transfer integral (half the bandwidth) in the perpendicular direction, and d is the QW layer period. The density of states corresponding to this equation is:

$$n(\epsilon) = \frac{m}{\pi^2 \hbar^2 d} \times \begin{cases} \cos^{-1}(1-\epsilon/t) & \epsilon<2t \\ \pi & \epsilon>2t \end{cases}$$

At temperature of absolute zero, impurities introduced by uniform or modulation doping yield carriers which fill the density of available states. For partial filling of the lowest miniband, the carrier density N corresponding to a Fermi energy E_F is

$$N = \frac{mt}{\pi^2 \hbar^2 d} \left\{ -(1 - \frac{E_F}{t}) \cos^{-1}(1 - \frac{E_F}{t}) + \left[2(\frac{E_F}{t}) - (\frac{E_F}{t})^2 \right]^{½} \right\}$$

The Seebeck coefficient (α) would then be:

$$\alpha = \frac{\pi^2}{3} k_B T \left[\frac{1}{n(\epsilon)} \frac{\partial n(\epsilon)}{\partial \epsilon} + \frac{1}{v^2} + \frac{\partial v^2}{\partial \epsilon} + \frac{1}{\tau(\epsilon)} \frac{\partial \tau(\epsilon)}{\partial \epsilon} \right]_{\epsilon = F_F}$$

where $n(\epsilon)$ is the density of states, v^2 is the square of the electrons velocity in the direction of external temperature gradient averaged over the Fermi surface $\epsilon = E_F$, and $\tau(\epsilon)$ is the energy-dependent momentum relaxation time.

Therefore from the above equation the change in Seebeck coefficient due to the effect of the thin film on the density of states could be written as:

$$\Delta\alpha = \frac{k_B}{e} \left\{ \frac{(E_g - E)}{k_B T} + 1 + \left[2 - (\frac{E_g}{k_B T})(\frac{I_0^2}{I_1^2}) \right] H \right\}$$

where E_g is the effective gap of the QW, therefore

$$E = K_B T \ln(\frac{\pi \eta^2 n_e d}{m k_b T})$$

and

$$H = \frac{[1 + (eE_0 d\tau)^2]}{[1 + 2eEd\tau)^2]}$$

where I_0, and I_1 are the modified Bessel functions of the argument E_g/k_BT.

The expression for $\Delta\alpha$ can further be simplified for the special case where $k_BT > E_g$:

$$\Delta\alpha = \frac{k_B}{e}\ln(\frac{T}{t})$$

where t is a characteristic coefficient which depends on the QW layers. Therefore:

For Hi-Z typical samples this generated the curve in Figure 4. The theoretical data match the experimental data very closely. This excellent match between the analytical and experimental data makes the model very viable for understanding the α behavior.

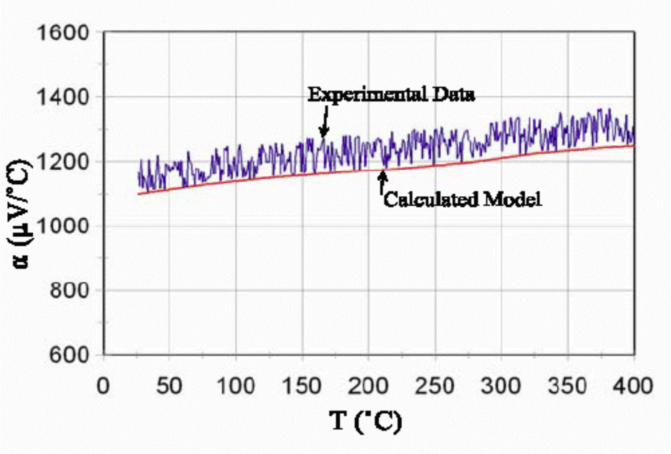

Figure 4. The Seebeck Coefficient versus Temperature. The calculated model matches the experimental data very closely.

QW Thermoelectric Device Life Test

Figure 5 shows a QW couple with B_4C/B_9C and Si/SiGe. An improved sputtering process was successfully developed to deposit the Mo metal contacts that exhibit a negligible contact resistance with both N and P material.

This QW couple was fabricated for life testing with N type Si/SiGe and P type B_4C/B_9C and operated for ~4,000 hours in a fairly stable mode and then degraded sharply to zero power the last few hundred hours, as shown in Figure 6. At cool down the N and P legs were no longer electrically connected. The ~2 μm thick Mo that joined the N and P legs on the hot side was not distinguishable. It may have fallen off the surface of the couple in its removal from the chamber and was lost.

Each leg was measured for α and ρ and essentially both legs remained constant in thermoelectric properties as shown in Table 2 indicating the degradation problem is all in the joint area.

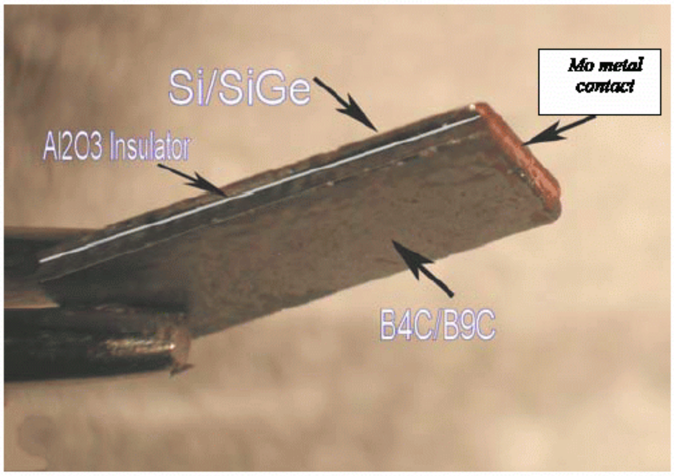

Figure 5. QW Si/SiGe-B_4C/B_9C couple for thermal stability test (0.2" x 0/8"). The Mo was deposited by an improved sputtering process. This is the first couple where an Al_2O_3 insulator was used (0.01" thick). The initial power generated agrees closely with that calculated from property data for the N and P materials.

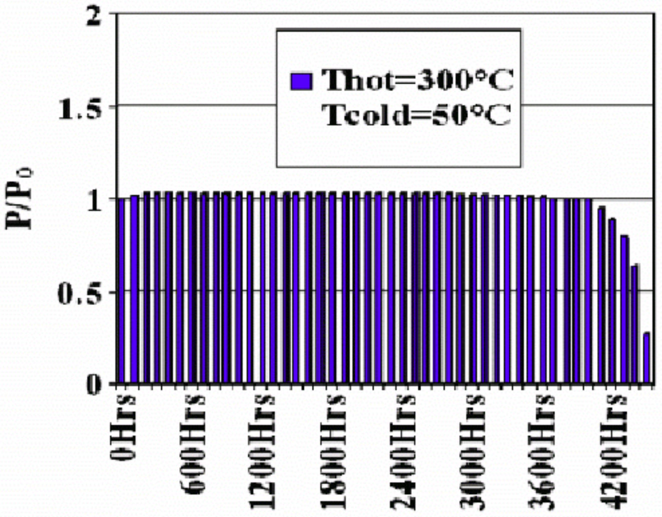

Figure 6. Life Test Data.

The N leg of Si/SiGe QWs and the P leg of B_4C/B_9C were examined on the SEM on cross section as shown in Figures 7 and 8. As can be seen the Mo was well bonded to the Si and SiGe layers in some areas while in other areas failure occurred primarily in the Si/SiGe right next to the interface, possibly due to thermal cycling or some of the Si/SiGe layers might have had microcracks induced during preparation of the sample that propagated during life testing and/or during periodic thermal cycling to room temperature to measure α and ρ, caused high thermal stresses. In future life testing the thermoelectric properties will be measured with the N and P couple at temperature.

Table 2. Measurements of Si/SiGe and B_4C/B_9C Legs Before and After Gradient Testing for ~4300 Hrs.

	Seebeck before aging	Seebeck after ~4,300 hours aging	Resistivity before aging	Resistivity after aging
Si/SiGe leg	~ -1260 μV/°C	~ -1220 μV/°C	~ 1.05 mΩ-cm	~ 1.1 mΩ-cm
B_4C/B_9C leg	~ +1120 μV/°C	~ +1090 μV/°C	~ 1.1 mΩ-cm	~ 1.2 mΩ-cm

Table 3. P type Si/SiGe Annealed at 1000˚C, 24 Hours Showed no Significant Change in Seebeck Coefficient and Electrical Resistivity.

	Seebeck Coefficient μV°C	Electrical Resistivity mΩ-cm
Before	~1000	0.75
After	~1000	0.76

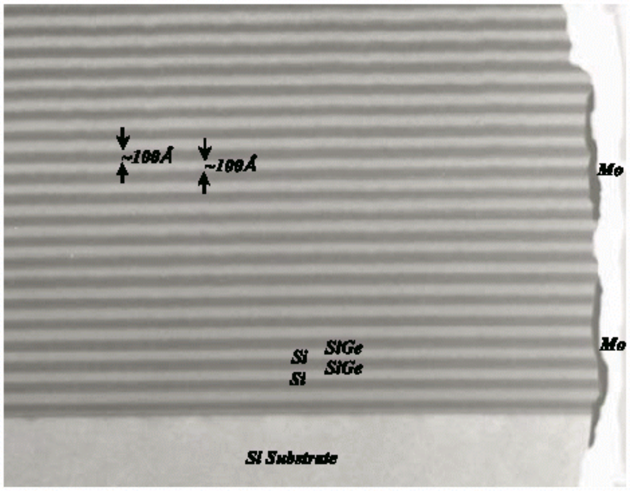

Figure 7. 150kX SEM of Si/SiGe leg of the ~4000Hrs aged couple.

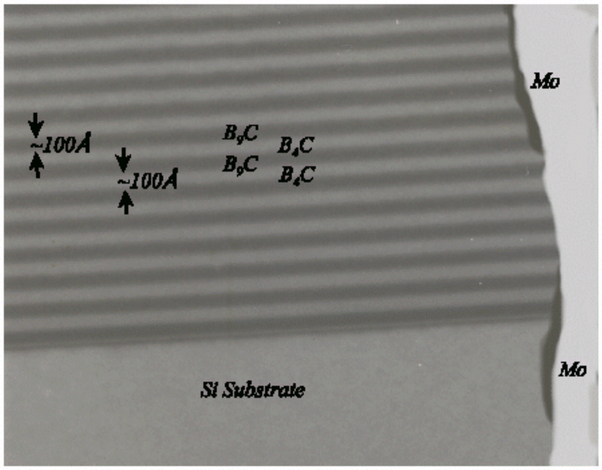

Figure 8. 150kX SEM of B_4C/B_9C leg of ~4000Hrs aged couple.

It was known before testing that thermal expansion differences among most of the components were quite small. However, the B_9C is known to be higher and may also initiated cracking during periodic thermal cycling. Future couples will have much thicker Mo than the ~ 2μm of Mo on this couple to provide more strength and not be as easily embrittled by diffusion of SiGe, B or C into the Mo.

Thermal Stability

A single crystal Si substrate coated with Si/SiGe QW films was subjected to a 24 hour anneal at 1000°C. The before and after Seebeck coefficient (α) and electrical resistivity (ρ) both before and after anneal is shown in Table 3 and indicates little or no change in thermoelectric properties. Previous longer term anneals, up to 600°C, also indicated no change in thermoelectric properties.

From all the isothermal and gradient thermal stability tests conducted thus far, there is no indication that these Si/SiGe QW films will degrade during operation as shown by the gradient data and the 1000°C-24 hours isothermal data shown in Table 3.

Conclusions

- The Si/SiGe and B_4C/B_9C QW materials continue to show promising thermoelectric performance, both as fabricated and when fabricated into a couple.
- A better understanding of the P type Si/SiGe films is needed as to why very low resistivities are obtained. A theoretical analysis of the calculated Seebeck coefficient data appears to agree with the data generated.
- Thermal stability of the QW films does not appear to be a problem based upon the experimental data generated with Si/SiGe and B_4C/B_9C.

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