EXPERIMENTAL STUDY OF THE EFFECT OF THE QUANTUM WELL STRUCTURES ON THE THERMEOELECTRIC FIGURE OF MERIT IN Si/Si$_{1-x}$Ge$_x$ SYSTEM

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ABSTRACT

In bulk form, Si$_{1-x}$Ge$_x$ is a promising thermoelectric material for high temperature applications. In this paper, we report results from an experimental study as well as theoretical modeling of the quantum confinement effect on the enhancement of the thermoelectric figure of merit. Si/Si$_{1-x}$Ge$_x$ multiple quantum well structures are fabricated using molecular beam epitaxy (MBE) on SOI (Silicon-on-Insulator) substrates in order to eliminate substrate effects, especially on the Seebeck coefficient. A method to eliminate the influence of the buffer layer on the thermoelectric characterization is presented. An enhancement of the thermoelectric figure of merit within the quantum well over the bulk value is observed.

INTRODUCTION

It has been shown theoretically [1] that it may be possible to increase the thermoelectric figure of merit (Z) of certain materials by preparing them in the form of two-dimensional (2D) quantum-well structures. This has already been demonstrated experimentally [2] using n-type PbTe/Pb$_{1-x}$Eu$_x$Te multiple-quantum-well structures grown by molecular-beam epitaxy.

In bulk form, Si$_{1-x}$Ge$_x$ is a promising thermoelectric material for high temperature applications [3-5], and has been used in radioactive-isotope thermoelectric generators (RTGs) on satellites and spacecraft for compositions of about Si$_{0.7}$Ge$_{0.3}$ operating at $\sim$1000 K [6]. Because of the large amount of expertise and information available regarding the materials science of fabricating Si/Si$_{1-x}$Ge$_x$ quantum wells, it is an interesting system for the demonstration of both proof-of-principle and 2D thermoelectric device operation at high temperatures. By carefully designing the Si/Si$_{1-x}$Ge$_x$ superlattice structures, we expect this system to have sufficiently good thermoelectric performance to be interesting for possible device applications.

TWO-DIMENSIONAL THERMEOELECTRICITY OF Si

The effect on Z of using materials in two-dimensional (2D) structures, such as 2D multiple-quantum-well (MQW) structures, has been studied earlier [1], and it was shown theoretically
Figure 1: (a) The 2D thermoelectric figure of merit for Si/SiGe superlattices as a function of sheet carrier density for various quantum well widths at $T = 300$ K, with the specularity $p = 1$. (b) The calculated $Z_{2D}(\zeta^*)$ versus carrier density at various temperatures (300 K, 400 K, ..., 900 K) for a 50 Å Si quantum well. The electron mobility is determined empirically as $\mu_e = 2.11 \times 10^8 T^{-1} \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ ($T$ in K) from data for bulk $n$-type Si with a carrier concentration of $10^{15} \text{cm}^{-3}$, appropriate for thermoelectricity applications.

that this approach could yield a significant increase in $Z$ over the bulk value as the quantum-well width is decreased. The proposed increase in the power factor $S^2\sigma$ arises mainly from the enhancement of the density of electron states per unit volume (near the Fermi level) that occurs for small quantum well widths. Further increase in $Z$ is possible through the reduction of the thermal conductivity, $\kappa$, resulting from enhanced phonon scattering at the interfaces between the quantum wells and barriers [7].

Si has six electronic ellipsoids along the [100]-axes of the Brillouin zone in the silicon conduction band. Each ellipsoid is characterized by the transverse ($m_\perp = 0.19 m_0$) and longitudinal ($m_\parallel = 0.92 m_0$) effective mass components. When quantized along the (100) direction, the mass anisotropy (roughly 4.5:1) causes different shifts of the longitudinal and transverse subbands due to their different effective mass components.

We considered an infinite series of quantum wells and barriers in a superlattice structure with a finite height of the barrier potential. Suppose the quantization is along the $z$-direction, then the subband minima are determined by

$$\left(\frac{\kappa^2 - k^2}{2\kappa k}\right) \sinh \kappa d_W \sin k d_W + \cosh \kappa d_W \cos k d_W = 1 \quad (1)$$

where $d_W$ is the width of the quantum well, $m_x, m_y$, and $m_z$ are the diagonal components of the effective mass tensor, $d_B$ is the width of the barrier layer, and $\kappa = (2m_U U/h^2 - k^2)^{1/2}$, in which $U$ is the height of the barrier potential and $k$ is the magnitude of the wave vector. The roots $\tilde{k}_n$ of Eq. (1) give the energy band structure as

$$E_n(k_x, k_y) = \frac{\hbar^2 k_x^2}{2m_x} + \frac{\hbar^2 k_y^2}{2m_y} + \frac{\hbar^2 k_z^2}{2m_z}. \quad (2)$$

Multiple band theoretical calculations of the power factor have been carried out as a function of the 2D carrier concentration for $n$-type Si, assuming that $d_B = 300 \text{Å}$ and
Figure 2: The structure of a set of three samples. Each period consists of a Si well and a SiGe barrier and is 35 nm wide. The three samples have 5, 10 and 15 periods, and are denoted as JL057, JL058 and JL059, respectively.

$U = 100 \text{ meV}$. For a multiple band model, the transport tensor is a linear combination of contributions from each transport subband. The overall electrical conductivity and Seebeck coefficient can then be calculated from

$$
\sigma = \sum_n \sigma^{(n)}, \quad S = \frac{\sum_n \sigma^{(n)} S^{(n)}}{\sum_n \sigma^{(n)}}.
$$

In a simple kinetic theory for phonon transport, the lattice thermal conductivity is determined by

$$
\kappa = \frac{1}{3} C v l
$$

where $C$ is the specific heat, $v$ the sound velocity, and $l$ the mean free path (MFP) for phonons. Such a treatment underestimates the MFP of those phonons that actually carry heat because (1) the optical phonons contribute to the specific heat but not much to the thermal conductivity due to their low group velocity, and (2) acoustic phonons in Si/SiGe materials have a large dispersion, so that their velocities are also smaller than the speed of sound. Therefore, we estimated the average phonon MFP theoretically by including only acoustic phonons and used an averaged phonon group velocity in Eq. (4) [8]. The interface scattering effect is also considered in the modeling of the Si/SiGe thermal conductivity. A parameter $p$ is introduced to characterize the specularity of the interface scattering, where $p = 1$ refers to pure specular scattering, while $p = 0$ refers to pure diffusive scattering [8]. It is shown that the reduction in thermal conductivity is significant even in the case of pure specular interface scattering ($p = 1$) [9].

The calculated two-dimensional thermoelectric figure of merit for Si/SiGe superlattices as a function of sheet carrier density for different quantum well widths at room temperature is shown in Fig. 1(a). Here we see that $Z_{TE} T$ within the quantum well can reach as high as 2.0 at room temperature for a superlattice with a quantum well width of 25 Å. This makes this system very interesting even at room temperature.

Since bulk Si/Si$_{1-x}$Ge$_x$ is a thermoelectric material that is aimed at high temperature operation (up to 1000 K), it is interesting to investigate the thermoelectric performance of Si$_{1-x}$Ge$_x$ quantum well systems at elevated temperatures. Since the power factor for Si$_{1-x}$Ge$_x$ materials generally increases with increasing $T$ above room temperature, the power
Table 1: Hall measurements of samples JL057-JL059 at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>JL057</th>
<th>JL058</th>
<th>JL059</th>
</tr>
</thead>
<tbody>
<tr>
<td># of periods</td>
<td>5</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>Mobility (cm²/Vs)</td>
<td>405.5</td>
<td>689.1</td>
<td>640.8</td>
</tr>
<tr>
<td>Sheet carrier density (cm⁻²)</td>
<td>$2.5 \times 10^{14}$</td>
<td>$5.17 \times 10^{13}$</td>
<td>$1.04 \times 10^{14}$</td>
</tr>
<tr>
<td>Sheet carrier density per period (cm⁻²)</td>
<td>$5.0 \times 10^{14}$</td>
<td>$5.17 \times 10^{12}$</td>
<td>$6.9 \times 10^{12}$</td>
</tr>
</tbody>
</table>

The factor as well as the thermoelectric figure of merit for Si₁₋ₓGeₓ quantum wells is expected to increase as T is increased above 300 K. By carefully considering the behavior of the carrier mobility as a function of temperature [7], we calculated the two-dimensional thermoelectric figure of merit as a function of quantum well width at elevated temperatures, as shown in Fig. 1(b). These results indicate that $ZT$ for Si/Si₁₋ₓGeₓ quantum wells is quite favorable higher temperatures.

**XPERIMENTAL STUDIES**

With low electrical conductivity has a very high Seebeck coefficient. It is therefore expected at the Si substrate as well as the buffer layer, which is essential to get the relaxed type-superlattice, might contribute to the transport measurements, especially to the Seebeck efficient measurement. Therefore, it is necessary to eliminate the contributions of the substrate and buffer layer to the measured transport coefficients, in order to make reliable measurements on superlattice samples. To eliminate the substrate contribution, we make use of Silicon-on-Insulator (SOI) substrates. In order to characterize the contributions to the measurements from the buffer layer, we grow a series of samples with the same structure, but with different numbers of periods. Three similar superlattice samples with 5 periods, 10 periods and 15 periods, respectively, were fabricated. Their structures are shown in Fig. 2, and are denoted as JL057, JL058 and JL059, respectively.

These samples were grown continuously, one after the other, using a solid source MBE system. Firstly, SOI wafers with 200 nm Si on top of 350 nm SiO₂ were used as substrates. After a standard Shiraki cleaning procedure, the substrates were immediately introduced to the MBE chamber. The protective oxide layer was removed by subsequently heating the substrates at 930 °C for 15 minutes. The growth temperature was kept at 550 °C except at the doped layers (Sb) were grown at 350 °C. The growth rate for Si and Ge were monitored and controlled by a Sentinel III Deposition controller. With these conditions, 100 nm of an undoped Si₁₋ₓGeₓ layer with x varying from 0 to 0.3 was grown first, on top of which a 100 nm layer of Si₀.₁Ge₀.₉ was grown, yielding a buffer layer with an overall thickness of 200 nm. Hall measurements (Table 1) show that these samples have a very similar sheet carrier density per period, which is essential to validate Eq. (5) that will be discussed below.

The Seebeck coefficients for samples JL057, JL058 and JL059 are measured with high precision at room temperature, as shown in Fig. 3(a)-(c). Least mean squared linear regressions are performed on the ∆V-∆T data to get the slopes for the Seebeck coefficients. The Hall offsets in the measurements suggest that we have achieved high quality electrical and thermal contacts in our measurements.

A simple calculation considering the contribution from both the buffer layer and the
Figure 3: The Seebeck coefficients for samples JL057, JL058 and JL059 are measured with high precision at room temperature, as shown in (a), (b) and (c), respectively. The measured Seebeck coefficient at room temperature as a function of $1/n$, where $n$ is the number of periods in each sample, is shown in (d). The Seebeck coefficient for the quantum well $S_w$ is extrapolated to the limit $1/n \to 0$, or $n \to \infty$.

Lattice to the Seebeck coefficient measurement shows that

$$S_n = S_w + \frac{R_w S_b}{R_b} \left( \frac{1}{n} \right),$$

where $S_n$ is the measured Seebeck coefficient for a sample with $n$ periods, $S_w$ and $S_b$ are the Seebeck coefficients for the quantum well and buffer regions, respectively, and $R_w$ and $R_b$ are resistances for the quantum well and buffer regions, respectively. Though $R_b$ is very large compared to $R_w$, $S_b$ is also very large due the low carrier density in the buffer layer. Therefore, the contribution of the second term could be significant. Figure 3(d) shows the room temperature results for samples JL057-JL059, and the Seebeck coefficient for the quantum well is extrapolated by setting $1/n \to 0$, or $n \to \infty$, whereas successfully eliminated the contribution from the buffer layer.

The power factor $(S^2 \sigma)$ at room temperature for this set of samples is found to be 45 $\mu$W/cm$^2$K$^2$, resulting in a two-dimensional thermoelectric figure of merit at 300 K of value
0.14, using the calculated value for the thermal conductivity, 9.64 W/mK, from our model as described above. Although this is a significant enhancement over the Si bulk value [7], we expect better performance if better carrier mobility (see Table 1) can be achieved by improving the interface quality.

CONCLUSIONS

Theoretical modeling of the thermoelectric figure of merit for Si/Si$_{1-x}$Ge$_x$ quantum well structures suggests that an increase in the thermoelectric figure of merit over bulk values in the Si/Si$_{1-x}$Ge$_x$ quantum well system should be possible. Further enhancement in $Z_{2DT}$ for Si/Si$_{1-x}$Ge$_x$ quantum well structures is expected at elevated temperatures through both quantum confinement and phonon interface scattering effects. Si/Si$_{1-x}$Ge$_x$ multiple quantum well structures are fabricated using the MBE technique, and the thermoelectric properties are successfully measured for a single period, after eliminating the contributions from the substrate and the buffer layer. An enhancement of the thermoelectric figure of merit in the quantum well over the bulk value in Si at 300 K is observed.

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