Quantum Modeling of Thermoelectric Properties of Si/Ge/Si Superlattices

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Abstract-- Using a non-equilibrium Green’s function (NEGF) approach, quantum simulations are performed to assess the device characteristics for cross-plane transport in Si/Ge/Si superlattice thin films. The effect of quantum confinement on the Seebeck coefficient and electrical transport and its impact on the power factor of superlattices is studied. In this case, decreasing well width leads to increased subband spacing causing the Seebeck coefficient of the superlattice to decrease. Electron confinement also causes a drastic reduction in the overall available density of states. Results show that confinement effects in the silicon barrier are responsible for a 40% decrease in the electrical conductivity of superlattices where barrier films are thinner by a factor of 1.5. In the same two devices, there is negligible change in the Seebeck coefficient, which results in a decrease in the power factor corresponding to the decrease in conductivity. This decrease in the electrical performance for superlattices with thinner layers may offset the previously hypothesized gains of highly scaled superlattice structures resulting from reduced thermal conductivity. Simulations of the present superlattice structure at varying doping levels show a decrease in power factor with a decrease in device size parameters.

Index terms--- Quantum confinement, thermoelectric, Non-equilibrium Green’s function

I. INTRODUCTION

The efficiency of thermoelectric materials is usually characterized by the dimensionless thermoelectric figure of merit $ZT = S^2\sigma T/\kappa$ where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity and $\kappa$ is the thermal conductivity. In the past decade, the use of confined structures such as quantum well and quantum wire superlattices have gained attention as thermoelectric materials due to a number of advantages. (1) The Seebeck coefficient can be increased by the increase in the local density of density of states per unit volume near the Fermi energy [1], and (2) the thermal conductivity can be decreased due to phonon confinement [2, 3] and phonon scattering at the material interfaces in the superlattice [4, 5, 6]. Normally, the electrical conductivity is assumed not to be significantly affected due to the large semiconductor bandgap and the disparity between the electron and phonon mean free paths [7]. The combined benefits of reduced thermal conductivity and improved Seebeck coefficient imply a theoretically higher $ZT$ compared to the bulk structures. However, experimental observations especially in the case of Si/Ge superlattices have not been able to achieve the presumed benefits of superlattice thermoelectric devices despite theoretically predicted improvements in $ZT$ and experimentally observed reduction in the thermal conductivity of superlattices compared to their bulk counterparts [1, 8]. Hence there is a need to better understand the effect of all the significant factors contributing to the thermoelectric figure of merit of nanoscale devices including the electrical conductivity, $\sigma$.

The dominant reduction in thermal conductivity in the superlattices is in the cross-plane direction [9, 10 and 11]. However, thermoelectric performance in the in-plane direction has been studied extensively mainly due to the difficulty associated with
conducting experiments in the cross-plane direction because of the very small film thicknesses and the effect of the large contact resistances [12, 13]. Interest in in-plane transport is also motivated by the higher mobility of electrons due to substrate strain [8, 14]. Yang et al. [12] measured the anisotropic behavior of in-plane and cross-plane superlattices and found that while the Seebeck coefficient did not change significantly, the electrical conductivity as well as thermal conductivity in the cross-plane direction is 5-6 times lower than the in-plane direction. The study of cross-plane transport in this paper is motivated by the higher decrease in thermal conductivity as well as the opportunity to study and understand quantum effects with a view to tune the electrical performance of superlattices by changing various parameters such as the thickness of layers, doping etc.

Experimental data of quantum effects on electrical conductivity is limited. However, the effect of confinement on electron mobility has been widely studied [15, 16]. It was found that intersubband scattering increased when the subband energy spacing for electrons was less than twice the polar optical phonon energy [17] leading to reduced electron mobility in confined structures. However recent theoretical studies of nanowires coated with an acoustically hard barrier shell [18] have predicted enhanced mobility of nanowires. Effects of confinement on the figure of merit have been studied as a function of the superlattice period in Ref. [19] using a constant relaxation time approximation model with a Kronig-Penny dispersion relation. Based on their calculations the value of $ZT$ reached a maximum limit as a function of the quantum well width. They theorized that for small barrier widths electron tunneling caused the value of $ZT$ to decrease while for large barrier widths the parasitic effect of backflow of heat from the barriers resulted in low $ZT$ values. It is clear from all the above studies that isolating and understanding the impact of quantum effects on the electrical conductivity and Seebeck coefficient are critical for the development of thermoelectric structures.

The most common method of predicting thermoelectric parameters is based on a semi-classical, relaxation time approximation model [1, 4, 5 and 6] where the system is assumed to be only slightly perturbed from equilibrium. Some of the early models employed parabolic energy dispersion for the conduction and valance band energies while later models incorporated the effect of low dimensionality through a subband energy dispersion relation [1, 4, 5 and 8]. Although these models use confined dispersion relations, transport and thermoelectric coefficients are still calculated using the semi-classical relaxation time approximation model that cannot adequately capture wave effects. Quantum effects such as tunneling are usually introduced in semi-classical models using correction terms [20, 21]. On the other hand, purely quantum transport models [22, 23] that involve the solution to the Schrödinger equation are limited to studying current flow where transport is generally ballistic or includes very limited scattering. In this regard the non-equilibrium Green’s function formalism provides a framework for coupling quantum effects and thermal effects to model electron transport in thermoelectric devices. Open boundary conditions allow the source and drain contacts to be coupled to the device through simple self-energy terms that eliminate the need for huge matrices that are of the size of the source and drain reservoir systems. Instead matrices in the NEGF formalism are the size of the device Hamiltonian. In addition, the NEGF formalism does not require a statistical distribution of carriers within the device thus allowing for the rigorous incorporation of both elastic and inelastic scattering effects using the concept of Buttiker probes [24]. A brief synopsis of the formalism is provided in the next section while a more thorough and detailed development can be found in Ref. [25].

In this work, the Green’s function approach is used to study the impact of electron confinement on the cross-plane thermoelectric properties of Si/Ge/Si quantum well superlattices with varying film thicknesses. As such, electron transport is modeled as purely ballistic neglecting scattering effects. We realize that additional effects such as electron-phonon scattering may influence the overall thermoelectric performance. The impact of electron-phonon scattering on thermoelectric properties have been studied using the NEGF method and can be found in our work [26, 27]. In that work, electrons in strained superlattices with structures similar to those studied in this paper are modeled to undergo both elastic and inelastic scattering with phonons. For the size of the superlattices considered, the
Seebeck coefficient does not change while the electrical conductivity showed a 43% to 64% decrease when electrons scatter with optical phonons. While incorporation of scattering effects is important to obtain a comprehensive prediction of the thermoelectric performance of nanostructures, the motivation of this paper is to model, isolate and understand quantum effects on the thermoelectric performance of nanostructured materials. As such, the assumption of ballistic transport does not limit the generality of the study of quantum confinement and tunneling on thermoelectric behavior in these devices.

II. THE NEGF FORMALISM

Consider the case of an open system consisting of a channel connected to source and drain contacts. Let $\mu_1$ and $\mu_2$ be the chemical potentials of the source and the drain. The distribution of electrons in the semi-infinite source and drain is said to follow the Fermi distribution. For a two-dimensional film the Fermi function is given by considering the electrons to have periodic boundaries in the infinite x and y directions and experience confinement along the z direction.

$$f_{2D} = N_0\ln(1 + \exp\left(-\frac{\epsilon}{k_BT}\right)) \quad \text{where} \quad N_0 = \frac{m^* k_BT}{2\pi h^2}.$$  \hspace{1cm} (1)

In the NEGF formalism the coupling of the device to the source and drain contacts is described using self-energy matrices $\Sigma_1$ and $\Sigma_2$. The self-energy term can be viewed as a modification to the channel Hamiltonian to incorporate the boundary conditions and can be written as

$$\left(H + U + \Sigma_1 + \Sigma_2\right)\psi_\alpha(r) = \varepsilon_\alpha\psi_\alpha(r). \hspace{1cm} (2)$$

The self-energy term $\Sigma$ originates from the solution of the contact Hamiltonian. In this semi-infinite system, which is connected to the channel, there will be an incident wave from the channel as well as a reflected wave from the contact. While the incoming electron from the contact will have infinite wave vectors in all three directions, the channel wave vector along the z-axis will occupy only discrete finite energy levels due to the formation of energy subbands along the z-direction. The wave function at the interface is matched to conserve energy. The energy conservation equation can be written as shown in equation 3.

$$E(k) = E_c + \frac{\hbar^2 k_x^2}{2m^*_x} + \frac{\hbar^2 k_y^2}{2m^*_y} + \frac{\hbar^2}{2m^*_z} \left(\frac{n\pi}{L_z}\right)^2 \quad \text{where} \quad n = 1, 2, 3, \ldots \hspace{1cm} (3)$$

The term $k_z = \frac{n\pi}{L_z}$ is the wave vector corresponding to the confined electrons that form discrete standing waves when confined in an infinite potential well.

The superlattice considered in this paper is modeled as a one-dimensional grid with a spacing of $a$ and the number of grid points $N$, such that the silicon film thickness is given by $L_{Si} = a(N_{Si} - 1)$. The thickness of germanium film is $L_{Ge} = a(N_{Ge} - 1)$. As the thickness of each layer changes the grid spacing is determined to ensure that the value of $t$ (equation 5 below) is always greater than the energy range of integration above the conduction band [25]. Electron transport is modeled in the cross-plane direction of the superlattice, which is also the confined direction. We use an effective mass Hamiltonian. The integration range for electron energy is from -1 eV to 1 eV over 1200 integration steps. The integration step size and lattice spacing were adjusted to ensure that convergence and grid independence were obtained.

The incoming wave vectors along the transverse x and y axes are taken to be equal to $k$ resulting in the boundary condition

$$\Sigma_i = -t \exp(ika) \hspace{1cm} (4)$$
where \( t \), the inter-unit coupling energy resulting from the discretization is given by

\[
t = \frac{\hbar^2}{2m^*a^2}.
\]

The source and drain self-energy terms are combined in the device Hamiltonian (equation 2) to solve for the energy eigenvalues in the channel from which the channel current is obtained. The entire calculation is carried out self-consistently with Poisson’s equation to account for the change in channel potential with the change in electron density. Doping for each film in the superlattice is applied by changing the relative energy between the Fermi level and the conduction band edge for each material using the relation [28]

\[
n = N_c \exp \left(-\frac{(E_c - E_f)}{k_B T}\right)
\]

III. RESULTS

The device under study consists of a single quantum well formed by alternating layers of silicon, germanium and silicon thin films as shown in Figure 1 with transport in the cross-plane direction. Electron confinement in the device occurs for two reasons. 1) The very small thickness of the films gives rise to discretely spaced energy subbands in the cross-plane z-direction. 2) For constant doping levels in all three layers, the larger bandgap of the silicon layers on either side of the germanium layer sets up a potential barrier for the electrons in germanium thus causing additional confinement of the electrons in germanium leading to a 1D potential well. Electron transport in the device under an applied bias is modeled along the confined z direction and the current is calculated over 10 subbands. The Seebeck coefficient for the well was studied for various temperature ranges of the source and drain contacts while varying the doping in the Si/Ge/Si well. The source temperature was maintained constant at 300K while the drain contact was maintained at a higher temperature relative to the source. The applied bias ranged from 0 to 0.1V.

![Figure 1. Schematic representation of a Si/Ge/Si quantum well superlattice modeled in the simulation.](image)

Figure 2 shows the cross-plane current-voltage characteristics for a ballistic Si(20Å)/Ge(20Å)/Si(20Å) quantum well doped to a concentration of \( 5 \times 10^{18} \text{cm}^{-3} \). The source-drain temperature difference ranges from 0K to a maximum of 30K. The higher temperature at the drain results in diffusion of electrons from the drain towards the source, opposing the direction of the bias leading to negative current values. As the applied bias is increased, more electrons from the source drift towards the drain and at a particular voltage, which we call the Seebeck voltage; the diffusion of electrons from the drain to the source is balanced by the drift current from the source to the drain leading to zero current. The Seebeck voltage obtained for each temperature gradient is divided by that value of the gradient to obtain the Seebeck coefficient.
Figure 2. Current density - voltage characteristics of a ballistic Si(20 Å)/Ge(20 Å)/Si(20 Å) quantum well structure. Channel temperature difference ranges from 0K to 30K.

Figures 3 shows the Seebeck coefficient of 6nm thick silicon films predicted using the NEGF model compared to values obtained from a relaxation time approximation (RTA) model [4] using a confined dispersion for electron confinement in the z direction. While we do not expect an exact match due to the very different nature of the two models, the Seebeck coefficient values from the NEGF model follow a similar trend as the RTA model.

Figure 3. Seebeck coefficient vs. doping for silicon films using the NEGF and a relaxation time approximation (RTA) model.

Figure 4 shows the electrical conductivity values as a function of doping for 6nm silicon film obtained from the NEGF and RTA models. Doping in both models is applied using Eq.6 by varying the relative difference between the Fermi level and conduction band edge. In addition, the RTA model requires the value of mobility in the direction of transport for electrical conductivity calculations. Because of the conflict in the electron mobility behavior with decreasing film thickness seen in the literature [15, 16, 17, 18], we use
the bulk mobility value of silicon as a benchmark for calculating the electrical conductivity using the RTA model. Despite the NEGF model treating electron transport as ballistic, the conductivity values predicted by the NEGF method are lower than the predictions of the RTA model. The lower conductivity values are attributed to the limited number of electron energy levels available for conduction in the 6nm film due to confinement effects that are captured by the NEGF model. These results support our hypothesis that confinement effects dominate at these size regimes.

Figure 4. Electrical conductivity vs. doping for silicon films using the NEGF and RTA models.

Figure 5 shows the cross-plane Seebeck coefficient values as a function of doping levels for Si/Ge/Si quantum well superlattices. The predicted Seebeck coefficient for each doping is an average of the value obtained for each temperature gradient. The results from our simulations are compared to measured values found in the literature. Considering the large spread in the experimentally measured values of the Seebeck coefficient for various doping levels our results are in fair agreement with the measured values. In addition, the trend predicted by the NEGF model match experimental data where increase in doping leads to reduced Seebeck coefficient. We do not expect our data to match experimental measurements exactly for a number of reasons that will be discussed later.
The NEGF method was used to compare the change in Seebeck coefficient due to confinement. For a constant silicon barrier thickness of 20Å, we compare the Seebeck coefficients by varying the germanium well thickness from 10Å to 20Å and 30Å. It can be seen from figure 5 that the calculated Seebeck coefficient values show a gradual increase in the Seebeck coefficient between the 10Å and 20Å and 30Å well sizes for a given doping level such that the difference in the Seebeck coefficients between Ge10Å well and Ge30Å well is approximately 30µV/K. The reason for the change in Seebeck coefficient can be understood by looking at the distribution for the available density of states per unit energy of the 10Å and 30Å wells seen in figure 6. In our simulations the major contribution to the current comes from the conduction band and the first subband. Since electrons from the contacts enter through silicon, the conduction band edge and first subband energies for silicon are also shown here by the dotted lines for reference purposes. To understand the theory behind the physics of the Seebeck coefficient consider the case of the Ge 10Å well. The density of states for the conduction band Ec has a value of 650eV\(^{-1}\), which is much higher than the value of 3eV\(^{-1}\) near the first subband E1. When the temperature at the drain is raised, the large number of electrons near the conduction band edge gain thermal energy and try to occupy higher energy levels. However, as the available density of states for E1 is much smaller than the states near Ec, very few electrons from the conduction band can occupy the states near the first subband E1. These drain electrons then diffuse to the silicon on the cold side filling its first subband. The drain electrons arriving at the source at energy E1 attempt to lose their thermal energy and to fall to the next lower energy corresponding to Ec. However, because most of the states near the conduction band at the source are already occupied, the hot electrons from the drain remain at the first subband energy E1 preventing additional drain electrons from diffusing towards the source, producing a voltage in the process.
Figure 6. Available density of states distribution vs. Energy for Si(20 Å)/Ge(10 Å)/Si(20 Å) and Si(20 Å)/Ge(30 Å)/Si(20 Å) superlattices. Ec\textsubscript{si} and E1\textsubscript{si} represent the conduction band and first subband energies in silicon respectively. All curves are plotted against the right axis except where noted.

While the Seebeck voltage is formed by a similar process in the Ge30Å case, the density of states at E1 is five times greater compared to the Ge10Å well. The larger density of states can be attributed to the fact that subband spacing in the Ge10Å film is greater than the Si 20Å film due to confinement effects of the thinner germanium film as shown in figure 7. As a result, for energy levels around E1, there will be very little contribution from the germanium film for electron transport. In the case of the Ge30Å superlattice, the subbands are more closely spaced leading to a greater contribution to transport and hence higher density of states around E1. While quantum confinement is commonly believed to increase the Seebeck coefficient due to increased density of states near the Fermi energy, this difference in the density of states near E1 between the two wells is the reason the Seebeck voltage is higher for the Si(20Å)/Ge(30Å)/Si(20Å) structure compared to the Si(20Å)/Ge(10Å)/Si(20Å) structure. Confinement effects were also studied for the case where the germanium well thickness was kept constant while the silicon barrier thickness was changed from 20Å to 30Å. In this case, the Seebeck coefficient was found not to be significantly affected by the change in barrier thickness. This behavior can be attributed to the fact that while the silicon barrier layers next to the source determine the supply of electrons into the superlattice, their diffusion and drift through the superlattice is governed by the density of states in the germanium well whose thickness is held constant in this case. Hence we see no change in the Seebeck coefficient with change in barrier thickness.

The electrical conductivity in the cross-plane direction of the superlattice films is calculated using the slope of the linear portion of the current density-voltage curve at 300K (seen in Figure 2). Figure 8 shows the change in electrical conductivity of the various superlattices with doping. For a constant silicon barrier thickness, the electrical conductivity for the superlattice films does not vary significantly with the change in the well thickness. The reason for this behavior is that the supply of electrons is governed by the silicon film thickness. If the germanium well is very thin, electrons can tunnel through germanium into the silicon film on the other side of the well while for large well thicknesses there will be sufficient density of states available in the germanium layer to contribute to electron transport. In addition, increase in doping also lowers the conduction band and subband energies providing more states for electron transport. The combination of quantum effects and doping resulted in a change of less than 5% in the electrical conductivity as a function of doping. However, for a constant germanium well thickness of 20Å when the silicon barrier film thickness is increased from 20Å to 30Å the electrical conductivity of the Si(30 Å)/Ge(20 Å)/Si(30 Å) structure increases by 40% compared to the Si(20Å)/Ge(20Å)/Si(20Å) superlattice. The increase in the conductivity with increase in barrier thickness is attributed to the closer
subband spacing of the 30Å silicon film compared to the 20Å film resulting in an increase in the density of states available for conducting electrons from the source.

![Figure 7. Band diagram for Si(20Å)/Ge(10Å)/Si(20Å) and Si(20Å)/Ge(30Å)/Si(20Å) superlattices showing conduction band and first subband energies.](image)

**Figure 7.** Band diagram for Si(20Å)/Ge(10Å)/Si(20Å) and Si(20Å)/Ge(30Å)/Si(20Å) superlattices showing conduction band and first subband energies.

**Figure 8.** Electrical conductivity vs. doping for Si/Ge/Si superlattices for varying film thicknesses. Experimental data (in filled circles and square) taken from [31 and 34].

The power factor $S^2\sigma$ was calculated using the electrical conductivity values and the Seebeck coefficient obtained for each doping level considered. Figure 9 shows the power factor values for each doping level as a function of the germanium well and silicon barrier film thicknesses. For constant silicon barrier thickness of 20Å, the increase in the germanium well thickness from 10Å to 30Å results in lowering of subband energies which results in a 6% increase in the Seebeck coefficient while the electrical conductivity shows a slight change. Accordingly, as seen from figures 5 and 8, the slight increase in Seebeck coefficient and electrical conductivity for the Ge30Å well case translates into a 12% increase in its power factor. Similarly, for constant germanium well thickness of 20Å, the thicker silicon 30Å barrier in the Si(30Å)/Ge(20Å)/Si(30Å) superlattice offers lower subband energies for electron transport from the source compared to the 20Å silicon barrier layer in the Si(20Å)/Ge(20Å)/Si(20Å) superlattice leading to a 40% increase in electrical...
conductivity. In this case, the Seebeck coefficient showed only a very small change due to the constant well thickness. The higher conductivity of the Si(30Å)/Ge(20Å)/Si(30Å) superlattice dominates the power factor resulting in a 36% increase in the power factor of this superlattice compared to the Si(20Å)/Ge(20Å)/Si(20Å) superlattice.

In addition to the effects of quantum confinement, the values used for the effective mass for silicon and germanium were found to have a significant effect on the predicted electrical conductivity values. For our calculations we used the effective mass corresponding to bulk conductivity values, but the various experiments in references 8, 30, 31 and 33 were performed on single crystalline epitaxial layers deposited on a graded SiₐGe₁₋ₓ substrate. For film thicknesses of the order of a few nanometers as used in our calculations, both silicon and germanium can be considered to be single crystals allowing us to use the effective mass for that particular orientation. In addition, the graded substrate used in the experiments introduces lateral strains in the silicon and germanium films causing changes in the band structure and the formation of barriers in the germanium film [1, 14]. While these effects are important and may affect the thermoelectric properties of the superlattice, this study is relegated to another effort [27]. The results obtained in this paper are significant in that they (1) demonstrate the capability of the NEGF method to model thermoelectric properties of quantum well superlattice structures and (2) allow us to isolate and study quantum effects on the thermoelectric performance of superlattices.

![Figure 9. Power factor vs. doping for superlattices with varying film thicknesses.](image)

IV. CONCLUSIONS

The nonequilibrium Green’s function method was used to successfully isolate and study quantum confinement effects on the cross-plane thermoelectric properties of a single period Si/Ge/Si quantum well superlattice. Confinement effects are captured in the form of increased subband spacing and a reduction in density of states available for electron transport between the superlattice layers. The net result is a decrease in the Seebeck coefficient of the superlattice as well as decreased electrical conductivity with confinement despite the ballistic nature of electron transport. This trend may explain why measured values of ZT have not been able to corroborate other theoretical predictions of improved performance with reduced sizes. Our quantum transport model has shown that there exists optimal values of well and barrier thicknesses below which confinement can prove detrimental to thermoelectric performance. These findings imply that the superlattice size parameters can be tuned for enhanced thermoelectric performance. The results of the device studied may not be directly generalizable to any superlattice structure and/or material because strain, band gap size, transport direction and effective mass, for example, will affect the magnitude and onset of confinement effects. Yet we expect the physical response due to
confinement (increased subband spacing, tunneling probability etc.) to be similar enough in other materials to show a decrease in performance with reduced layer size. Finally, even though a single property cannot be considered in isolation for optimal performance, overall, the capability of the NEGF method as a platform to design structures with enhanced figure of merit has been established.

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