Quantum Simulation of Nanocrystalline Composite Thermoelectric Properties

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Abstract

The electrical transport properties of semiconductor nanocrystalline composite (NCC) thermoelectric structures were studied from a quantum point of view using a 2D non-equilibrium Green’s function (NEGF) computational approach. Previous researchers have shown enhancement in thermal properties of NCC devices but have not extensively studied their electrical transport properties for increased thermoelectric performance. The NCC structure was parametrized to determine the performance as a function of crystal spacing and crystal size. Results indicate that a silicon matrix (well) and a germanium crystal (barrier) configuration results in largest Seebeck coefficient. Power factor of NCC devices were compared to equivalent superlattice devices, and greater performance was shown for equivalent NCC characteristic lengths.

1 Introduction

Nanostructured materials have been proposed and applied by many researchers [1, 2, 3, 4, 5] to improve the thermoelectric efficiency over bulk materials. Recent studies of nanocrystalline com-

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posite (NCC) structures composed of embedded nanoparticles in crystalline semiconductors have shown promising transport properties related to thermal conductivity \([2, 6]\), suggesting they are indeed candidates for nanostructured materials with enhanced thermoelectric properties. However, their corresponding electrical transport properties have yet to be studied extensively.

Conventional wisdom suggests that improving the electrical properties is less rewarding than increasing the thermal properties due to the large band gap of many thermoelectric materials. This assumption is based primarily on bulk materials and particle based theory, as opposed to a wave-based theory for confined structures. Both the optimization of thermal and electrical transport properties are important in constructing an efficient direct energy conversion device. Even though both the electrical and thermal properties are important, this work will focus on only the electrical contribution to the overall ZT. The following research approaches the calculation of the electrical properties through a two-dimensional wave-based computational model, paying particular attention to the geometric aspects of NCC’s. Of interest are three basic parameters of NCC structures: 1) band structure originating from the crystal and matrix material, 2) crystal spacing, and 3) crystal size.

The performance of thermoelectrics is commonly quantified by a dimensionless figure of merit \((ZT)\), defined as

\[
ZT = \frac{S^2 \sigma T}{k_e + k_p}
\]

where \(T\) is the average temperature, \(S\) is the Seebeck coefficient and \(k_p\) is the lattice contribution to thermal conductivity. The objective is to maximize \(ZT\) by either maximizing the power factor \((PF = S^2 \sigma)\) or minimizing the denominator. The electrical conductivity \((\sigma)\) and electron thermal conductivity \((k_e)\) are proportional because of the Wiedemann-Franz law, which suggests optimization should be focused around increasing the Seebeck coefficient.

Several studies \([7, 8, 2, 9]\) have shown increases in the figure of merit through incorporation of defects, inclusions and nanoparticles in hopes of decreasing the phonon thermal conductivity \((k_p)\). Kim, et al. \([2]\) have experimentally studied embedded nanocrystals in a matrix material and saw a noticeable decrease in the thermal conductivity. Their experimental studies attribute the decrease in thermal conductivity to three factors, the most significant being the increased phonon scattering.
as a result of the nanocrystal being on the order of the mean free path.

Jeng, et al. [9] studied similar thermoelectric Si/Ge embedded nanoparticle materials using a Monte-Carlo model to determine the thermal conductivity and noted that select materials with nanoparticles on the order of 10 nm could outperform the alloy of the constitute material. They also noted that the aligned particles resulted in a lower thermal conductance compared to randomly dispersed nanoparticles.

Only a select number of researchers have studied the electronic effects of nanocrystals in thermoelectric devices. Many of these studies are for randomly dispersed nanocrystal and very few have investigated nanoparticles. Wang [5] has experimentally studied free-standing PbSe nanocrystal thermoelectrics as a function of crystal size and has attributed an increase in electrical transport to confined states that are delta-like in shape, which are shifted closer or further from the conduction band edge depending on the size of the nanocrystals. To support Wang’s qualitative explanation of shifted density of states, this effect is captured inherently in the quantum model presented in the foregoing research.

Other researchers such as Zeng [10] experimentally studied the cross-plane electronic transport effects of nanostructures and noted a increase in cross-plane Seebeck when inclusions were added. Zide [11] attributed the increase in Zeng’s experiment to an electron filtering phenomenon and thermionic emission in the cross-plane direction. While their trends are commensurate with measurements, the magnitudes of the conductance in their Boltzmann-based type model is dependent on user specified scattering time, which is essentially a fitting parameter. These fitting parameters suggest large uncertainties for devices not experimentally tested. The modeling approach in the present study attempts to predict the transport from more fundamental quantities namely band offset and effective mass described from a quantum point of view. Along with describing the structure from a wave-based model, nanoscale transport phenomena such as tunneling and confinement are captured without special treatment.

Because the nanoparticles are nanometers in diameter and the spacing between nanoparticles is nanometers there is inherently confinement on energy levels within and between nanoparticles. The confinement of energy levels is a result of the quantization and follows the relation, \( \frac{\hbar^2}{2m^*a^2} \).
Researchers[12] have shown that confinement is a relevant quantum effect that must be accounted for in nanoscale transport. The selection of a NEGF model over drift-diffusion or Monte-Carlo is solely based on being able to capture the quantum effects, which are not inherently available in continuum or particle type models without correction terms.

2 Material and Methods

The simulated NCC devices in this study were modeled from the experimental construction of NCC devices [2], shown in Figure 1. Due to the periodic nature of the structure, the computational domain was reduced to the smallest repeated structure of the material, which contains a single crystal surrounded by matrix material. The device was confined in the in-plane and cross-plane directions with an infinite extent in the vertical (out of plane) direction. The geometry of the crystal was approximated to have a square cross-section because then the interface of the matrix material and the crystal material lie at cell boundaries in a rectilinear mesh, which simplifies the computation. Nevertheless, we contend without evidence that by assuming a square cross-section the transport is underestimated due to the neglect of glancing incidents from electrons interacting with a circular cross-section.

The computational method employed to calculate the electrical transport properties of these
devices is a self-consistent Schrödinger-Poisson type solver. A non-equilibrium Green’s function (NEGF) computational method [13] was implemented to solve the two-dimension Schrödinger wave equation. An effective mass Hamiltonian is used to describe the dynamics of the electrons. The 2D Hamiltonian takes the following form,

\[ H \psi = -\frac{\hbar^2}{2m^*} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \psi = \epsilon_n \psi_n, \]  

(2)

Because the transport is along two directions the remaining out-of-plane spatial direction is assumed infinite. Additionally, because only a single crystal is modeled the boundaries in the transverse direction are assumed periodic and handled through modification of the Hamiltonian. The periodic boundaries in the transverse direction account for the interaction of neighboring crystals.

The transport is governed by the Landauer formalism,

\[ I_{\text{tot}} = \int^{E_{\text{max}}}_{E_{\text{min}}} \frac{2e^2}{\hbar} \Xi (f_2 - f_1) dE, \]  

(3)

which states that the total current is proportional to the quantum conductance, \( \frac{2e^2}{h} \), times the transmission probability, \( \Xi \), times the difference in Fermi energy, \( f_2 - f_1 \), integrated over energy. From this relation the current voltage (IV) characteristics of each device is determined.

This model has been used in previous research [1, 14] to study the electrical transport in superlattice thermoelectric structures with good agreement given the available experimental data. The only modification of the code from these previous experiments was to incorporate a two-dimensional effective mass Hamiltonian along with an Anderson mixing technique [15] to increase the rate of convergence of Poisson’s equation. Because the out of plane (z-direction) is infinite the Hamiltonian is integrated such that the units of energy are per length. This forces the electronic transport to be in the computational plane.

The modeling approach is based on calculating the steady state probability of single electron carriers through a self-consistent field. The contacts in the longitudinal directions are assumed infinite in extent where the analytic wave solution can be determined along with electron distribution, which is a function of both temperature and applied voltage. The objective of the model is
to determine the transport based on a composite system defined by the two longitudinal infinite contacts and the channel region. The wave functions within the channel region, which ultimately govern the transport, are calculated at independent energy levels integrated over the appropriate energy range. To account for the interaction of many electrons in the system the model employs a self-consistent field approach that calculates Poisson's equation from the charge distribution originating from the superposition of wave functions. This model assumes that the potential varies smoothly within the channel region, and the explicit electron pair interactions are accounted for in the self-consistent term. The electrons are assumed degenerate and spin independent and only the wave functions of the well defined delocalized conduction electrons are of interest in this model. The self-consistent field method used in the model is an appropriate single-carrier model because the interaction potential is less than the mean thermal energy ($k_B T$). In the case where this condition is not met, a more rigorous model would be necessary to resolve effects such as Coulomb blockade.

The Seebeck coefficient is calculated directly by opposing the thermal current with an applied voltage. First a temperature difference is applied between the contacts, which induces a current because of the difference in the Fermi distributions. Then a bias is applied that opposes the thermal current. The applied voltage that results in a net zero current is considered to be the Seebeck voltage. The Seebeck coefficient is the imposed temperature difference divided by the Seebeck voltage. The power factor is the product of the Seebeck coefficient squared times the electrical conductivity. All the results are based on ballistic electron transport with self-scattering contacts [1, 13]. Bulusu et al. [16] has shown in their study of non-coherent electron transport of similar dimension superlattice structures that transport is ballistic and scattering can be neglected for devices of this scale. Experimental studies of single crystalline silicon [17] demonstrated for n-doped Si, the mean free path of electrons at 300 K is on the order of 20-30 nm. Because the devices of interest are less than the mean free path of electrons, the devices of interest are assumed to be within ballistic transport regime. As the unit cell description is scaled to device sizes greater than the mean free path, electron-phonon interaction will decrease the electrical transport but will be on the same order of magnitude for all devices. Therefore we assume that optimization of the relative transport properties in the ballistic regime will correlate to the non-ballistic regime.
<table>
<thead>
<tr>
<th>Device</th>
<th>Matrix Material E_c [eV]</th>
<th>Crystal Material E_c [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-Ge</td>
<td>0.186</td>
<td>0.602</td>
</tr>
<tr>
<td>Ge-Si</td>
<td>0.160</td>
<td>-0.266</td>
</tr>
<tr>
<td>Si-Si</td>
<td>0.186</td>
<td>—</td>
</tr>
<tr>
<td>Ge-Ge</td>
<td>0.160</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 1: Strained conduction band edge of silicon and germanium for different material configurations. Fermi energy = 0.1eV

The material selection for the simulations were crystalline (100) silicon (Si) and germanium (Ge). Selection of these materials were based on the well-characterized material properties of silicon and germanium and abundance of experimental data in the literature. Given both Si and Ge have the same crystalline structure and the assumption that the transport is in the (100) plane, the only modification to the band structure as a result of interfacing the two materials is lattice mismatch. The difference in lattice constant results in localized strain at the material interface that can be corrected through modification of the band structure. The modification of the conduction band edge is a band offset either positive or negative depending on whether it is tensile or compressive strain. The magnitude of the band offset is estimated using tabulated deformation potential [18]. For all devices studied in this research, the conduction band edge of the crystal material is strained throughout the thickness. Table 1 outlines the corresponding conduction band edge for silicon or germanium due to straining effects. For a device with a silicon matrix and germanium crystal (Si-Ge), the conduction band edge of the silicon is lower than the germanium conduction band edge of 0.602eV. Because the strained germanium conduction edge is much greater than that of silicon, the device forms a deep electron well in the silicon material; this may also be seen as a large electron barrier in the germanium. If the crystal material and matrix material are transposed, a Ge-Si structure is formed where a deep electron well forms in the silicon crystal, and the conduction band edge lies below the Fermi energy of 0.1eV resulting in degeneracy of the silicon. The degeneracy leads to sensitivity of the Seebeck and electrical conductivity, which is seen in Figure 2. All devices in this study are n-type with dopant concentration held at $10^{18}$ cm$^{-3}$.

To validate the model, calculated values for homogeneous silicon and germanium were compared to experimental n-type bulk values from available literature at 300 K and a dopant concentration
of $10^{18}$ cm$^{-3}$. Table 2 outlines the comparison of values from the literature and the experimental results. Si and Ge values furthest right in Figure 1 and Figure 2 are assumed bulk equivalent.

<table>
<thead>
<tr>
<th>Material</th>
<th>Experimental</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>750[19]</td>
<td>1000[17]</td>
</tr>
</tbody>
</table>

Table 2: Model validation of experimental and calculated bulk values at a dopant concentration of $10^{18}$ cm$^{-3}$ and a temperature of 300 K.

3 Results and Discussion

The NCC device was analyzed by simulating a range of lengths by incrementally increasing the crystal spacing and crystal diameter respectively. Figure 2 depicts the Seebeck coefficient and electrical conductivity of homogeneous silicon (Si-Si), homogeneous germanium (Ge-Ge), silicon matrix germanium crystal (Si-Ge), and germanium matrix silicon crystal (Ge-Si) devices as a function of total device length. In this set of simulations the thickness of the matrix material ($L_m$) and diameter of crystal material ($D$) are increased by 0.2nm for each data point. The Seebeck coefficient is greatest for a silicon matrix, germanium crystal (Si-Ge) device as a result of the electronic band structure. The Si-Ge device can be thought as forming a classic quantum well-barrier structure, in which the conduction band offset between the germanium conduction band edge and the silicon conduction band edge is finite. The Seebeck performance is dependent on the equilibrium position ($I = 0$) which is largely influenced by the low lying electron states in the electronic well (silicon layer for this configuration). A large build up of charge forms on either side of the barrier leading to non-uniform distribution of charge. This charge build up as a result of the barrier is beneficial from the point of view of increasing the Seebeck coefficient but is an obstacle for the electrical conductivity. The electrons either have to gain energy to go over the barrier or tunnel through the barrier, which is a function of the barrier length. In turn, the electrical conductivity is greatest for the homogeneous germanium device due to the absence of a barrier and the low conduction band edge (0.160 eV). The crystal (barrier) is essential for increased Seebeck coefficient but can also be tuned through mindful selection of crystal size for good electrical conductivity.
Figure 2: In-plane Seebeck and electrical conductivity for increasing device length. The matrix thickness ($L_m$) and crystal diameter are increased by 0.2 nm and the device length ($L$) across the midspan is equal to two times the matrix thickness plus the crystal diameter ($2L_m + D$).

The large increase in conductivity in Figure 2 for the Ge/Si devices is a result of the alignment of energy levels as the device length increases. As eluded to in Equation 2, the energy levels follow the relation, $\frac{\hbar^2}{2m^*a^2}$, where $a$ has units of length related to the thickness of either the barrier or well region. Assuming the lowest lying conduction band edge of the barrier and well are located at a different energy, as the length of the barrier and well increases the energy levels will collapse as a result of decreased degree of confinement. Illustration of the energy levels collapsing is shown in Figure 3. The increased transport is only apparent in the well case (Ge/Si device) due to the alignment of energy levels at conduction band minimum of the matrix material. In Figure 2, the conduction increases dramatically at $L = 2.5$ nm and again at $L = 4.5$ nm. Both increases are characterized by electronic energy levels becoming aligned. Away from these thicknesses, levels are not aligned and the conduction is less. In the case of the Si/Ge device, where an electronic barrier is formed by the crystal material, the transport of the electrons in the low lying conduction band of the matrix material is always influenced by the barrier of the crystal and prevents the alignment of energy levels across the device at conduction band minima of the matrix material.

For the remainder of this article, we assume that the device is constructed from a silicon matrix with a germanium crystal based on the aforementioned Seebeck performance.
Figure 3: Illustration of the discreet energy level confinement within the crystal and between
crystals as a result of spatial dimensions. As the spatial dimensions increase confinement is relaxed
and energy levels collapse (in the direction of the arrows) providing possible alignment of energy
levels across the device leading to increased electrical conductivity. The model explicitly calculates
the confinement of discreet energy levels by solving the eigenvalue solution of the unperturbed
effective mass Hamiltonian.

3.1 Crystal Spacing

Constraining the crystal diameter (D) and increasing the crystal spacing, Figure 5 shows the cor-
responding Seebeck and electrical conductivity trends. Extrema in the Seebeck coefficient exist
for devices with crystal diameter between 1.5nm and 2nm. For the 1.5nm crystal diameter, the
maximum Seebeck coefficient lies where the gap between crystals is equal to 1nm. These extrema in
the Seebeck can be attributed to a critical distance from the neighboring crystals in which discrete
energy levels (eigenvalues) of the system diverge. As the spacing between crystals increases, the
energy levels collapse, forming a large localization of energy levels which are occupied by conduction
electrons. If the crystal spacing decreases, the energy levels separate relative to each other forming
widely spaced discrete energy levels. The shifting of energy levels limits the density of states below
the conduction band edge of the barrier (0.602eV), inducing a filtering effect from the barrier [11].
This filtering effect limits the conductivity and alters the local density of filled electrons, ultimately
influencing the Seebeck coefficient. The low lying energy states are visualized in Figure 4 in the
plot of the local density of available states (LDOS) as pockets of states to the right and left of the
barrier. In Figure 4 there are no states within the crystal (barrier) region, which ultimately induces
the filtering effect. Also, the low lying states next to the barrier are the states that contribute the
most to the tunneling current because they lie within $k_B T$ of the conduction band edge of the
matrix material.
Figure 4: Local density of available states (LDOS) along the centerline in the cross-plane (transport) and in-plane (perpendicular transport) directions. Note the low lying states in the matrix (well) material. The device is a 2nm silicon matrix with a 1nm germanium crystal.

Figure 5: Seebeck and electrical conductivity for increasing crystal spacing (Lm) and constant crystal diameter (D). Silicon matrix germanium crystal (Si-Ge) device. Locus exists in the Seebeck coefficient for devices with crystal diameters between 1-3nm.
3.2 Crystal Size

To study the relationship of crystal size on the electrical transport, the total device length \((L)\) was held constant and the crystal diameter \((D)\) was increased (Figure 6). The Seebeck coefficient increases as the crystal size increases; however, the electrical conductivity decreases at a much greater rate. Again, as the crystal increases in size it acts as a filtering mechanism and forces electrons to either transport around or tunnel through the crystal (barrier). The increased Seebeck is a result of the electron distribution below the crystal conduction band edge and is a function of energy levels within the electronic well region. The electrical conductivity decreases as the crystal size increases due to the decreased tunneling probability and the limited transport by low lying energy levels around the crystal. As the crystal diameter increases, the low lying energy levels in the matrix diverge limiting the number of states forcing electrons to higher energy states and decreasing conductivity. Because the conductivity decreases at a much greater rate than the Seebeck increases, the optimal power factor is obtained with a small crystal size.

3.3 Superlattice Comparison

In the limit of large crystals or small crystal spacing, the nanocrystalline composite approaches the geometry of a superlattice. Therefore, a comparison of the power factor (PF) of nanocrystalline...
Figure 7: Power factor plot comparing superlattice device to a nanocrystalline composite device for increasing germanium barrier thickness. Greater efficiency can be achieved with NCC at equivalent SL device sizes.

composite (NCC) devices to that of a superlattice (SL) device was carried out for a range of geometries (see Figure 7). The thickness of the barrier material in both the SL and NCC device was chosen as the independent variable while maintaining an equivalent characteristic length. The characteristic length of both devices is defined as the distance between contacts in the transport direction. The superlattice results were calculated using a similar computational method described by Bulusu et al. [1, 14].

In Figure 7, as the barrier thickness increases, the superlattice power factor decreases at a much faster rate than the nanocrystalline device. As discussed in previous sections of this article, the rate at which the NCC device decreases is governed not only by the probability to tunnel through the barrier but to also transport around the barrier. The SL device, on the other hand, is governed only by the probability of tunneling through the barrier.

4 Conclusion

The following research implemented a 2D NEGF method to calculate the transport properties of nanocrystalline composite thermoelectric material with particular emphasis on geometric effects. Findings from this work identified four design rules for designing an optimal NCC thermoelectric material: (1) A composite structure with silicon as the matrix and germanium as the crystal has
the greatest Seebeck coefficient compared to any other silicon-germanium material combination. Therefore better performance can be obtained when the nanocrystal forms an electronic barrier. (2) A optimal crystal diameter was determined to be as small as possible to induce moderate filtering of electrons while still maintaining a high electrical conductivity. (3) Results suggest crystal spacing is more influential on transport properties than crystal size, which suggests that designers should minimize crystal size and select a spacing equivalent to the diameter. (4) NCC devices have greater power factors than an equivalent superlattice structures, resulting in a thermoelectric material with greater performance per unit area. Compounding these findings with the decreased thermal conductivity of NCC devices by other researchers, NCCs prove to be viable direct energy conversion material.

References


[11] JMO Zide, D. Vashaee, G. Zeng, JE Bowers, A. Shakouri, and AC Gossard. Demonstration of electron filtering to increase the seebeck coefficient in ErAs: In0.53Ga0.47As/In0.53Ga0.28Al0.19As superlattices. *Physical Review B*, 74:205335, 2006.


