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QUANTUM SIMULATION OF NANOCRYSTALLINE COMPOSITE THERMOELECTRIC PROPERTIES

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ABSTRACT

For the past few years, nanoscale structures have been proposed and investigated experimentally for their enhanced thermoelectric properties over bulk materials. These structures offer several advantages: 1) increased local density of states, which can improve the Seebeck coefficient and 2) reduced thermal transport due to phonon confinement and increased scattering. Recently, nanocrystalline composites (NCC) have been examined for their ability to outperform the alloy limit in terms of reduced thermal conductivity. However, the electrical performance has not been examined from a quantum point of view. This work provides quantum simulations of a two-dimensional composite system meant to model certain geometric features of NCC's. While the results cannot be quantitatively compared to actual measurements, they show how their electrical behavior differs from well-known superlattice devices. This work will aid in the design of the next generation of NCC devices for thermoelectric performance.

NOMENCLATURE

d Diameter (nm)
l Length (nm)
T Temperature (K)
S Seebeck (μ V/K)
σ Electrical Conductivity (1/Ω-m)
PF Power Factor (W/m^{2}K)
ZT Thermoelectric Figure of Merit
k Thermal Conductivity (W/m^{2}K)

INTRODUCTION

An understanding of the quantum transport properties of nanostructured materials is critical in optimizing the performance of such structures. The application of nanostructured devices has been proposed and studied by many researchers over the years [1, 2]. Recent study of nanocrystalline composite (NCC) structures has shown promising quantum properties superior to those of bulk materials. One of the pressing applications for such nanostructured materials is in direct energy conversion devices such as thermoelectrics.

Researcher have studied NCC structures both analytically [3] and experimentally [4] from a thermal transport point of view but have not extensively studied their electrical transport properties. Common wisdom suggests that increasing the electrical properties is less rewarding than increasing the thermal properties due to the large band gap of thermoelectric materials. This assumption was primarily gathered from bulk materials and particle based theory, as opposed to wave based theory. Both the optimization of thermal and electrical transport properties are important to constructing an efficient direct energy conversion device. The following research approaches the understanding of the electrical properties through a two dimensional wave based computational method.

The study of such NCC structures requires a quantum point of view to fully grasp the quantum effects at a small scales. In order to capture the quantum effects, a wave based model was con-

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structed and implemented using a non-equilibrium Green's Function (NEGF) method. The same method used in the following research was rigorously applied to study the electrical transport properties in superlattice devices [5]. These superlattice structures prove to be very similar in nature to NCC structures, only NCC structures have a more complex geometry and added direction of confinement. Previous research of superlattice devices suggested that quantum confinement effects and increased density of state per unit volume led to altered thermoelectric properties.

Basic theory of bulk semiconductors describes the electrical properties to only be a function of material characteristics such as dopant density. It is not always apparent that commonly intensive properties (e.g. conductivity) of bulk materials become extensive on the nanoscale due to the introduction of quantum effects. This knowledge introduces additional design parameters that can be exploited to increase electrical properties of nanoscale devices. The following research focuses on three basic parameters of NCC structure: 1) crystal and matrix material, 2) crystal spacing, and 3) crystal diameter. It will be shown that electrical properties can be significantly altered based on these parameters.

ANALYSIS

0.1 Nanocrystalline Composite Construction

The theoretical construction of NCC devices studied in this research were modeled from the approximate construction of such experimental devices [3], shown in Figure 1. Due to the periodic nature of the structure, the computational domain was truncated to a unit cell of the material containing a single crystal surrounded by matrix material. The extent of the device was confined in the longitudinal and transverse direction with an infinite extent in the vertical. Furthermore, the unit cell domain was geometrically constrained to have a square geometry, where the total length (longitudinal transport direction) of the device was equal to the height (transverse transport direction). Additionally, the geometry of the crystal was approximated to have a square cross-section, opposed to a round cross-section found in the actual structure. The square geometry of the crystal allows the interface of the matrix material and the crystal material to lie at cell boundaries in a rectilinear mesh.

The material selected for computational analysis was (100) unstrained silicon and germanium. The follow parameters are described in Table 1.

0.2 Computational Method

Nanoscale electrical transport is based on quantum effects and limits the ability of particle base models to capture the underlying transport mechanisms. In order to capture such effects, a wave based model must be implemented. The Schrodinger equation, which describes the wave nature, was solved using a non-equilibrium Green's function (NEGF) method. This method has been used previously to study quantum effects [6] with good agreement; a formal presentation of the method can be found in [7, 8].

Table 1. Material parameters used in the NEGF model

Effective mass of silicon	$0.91m_e$
Effective mass of germanium	$0.95m_e$
Relative permittivity of silicon	11.7
Relative permittivity of germanium	16
Grid Spacing	1 Å

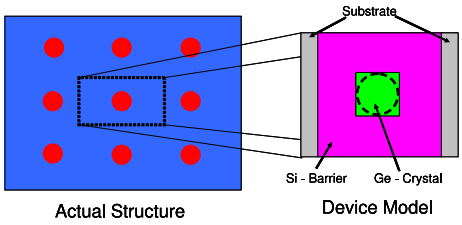

Figure 1. Unit cell representation of nanocrystalline composite structure.

A two dimensional effective mass Hamiltonian was constructed that averages the effects of the periodic potential of the lattice. Likewise, a two dimensional discretization control-volume approach was employed that required the material interfaces to lie at the nodes to ensure the Hamiltonian was Hermitian. The grid spacing was chosen so the solution was grid independent and converged. The model uses a self-consistent source and drain region that were considered ohmic contacts. Additionally, the top and bottom of the domain were assumed reflective. For the devices studied in this research, electrons transport across the device is ballistic and scattering is not of concern for small mean free path to device length ratios. It should also be noted that straining of only the crystal material is also incorporated into the model as a result of different lattice constants of the two materials [9].

The calculation proceeds by applying a temperature difference across the device generating a voltage between source and drain contact regions causing an increase in the occupancy of states, as described by Fermi-Dirac statistics. Broadening of energy level form at the source that extends into the device, resulting in a greater current transported across the device. The subband energy levels of the system are determined by solving for the eigenvalues of the Hamiltonian. Due to the geometric confinement in the longitude and transverse direction, the energy levels are limited. Using these discrete energy levels a one-energy level channel approach [8] can be used to sum across all energy level to get the net current flow. A source and drain voltage bias is incrementally increased in the opposing thermal gradient di-

rection until the net current becomes zero. From the determined current voltage relationship, the Seebeck coefficient, described by the x-intercept of the I-V curve and the electrical conductivity, defined as the slope of the I-V curve can be determined for a particular device.

RESULTS

0.3 Matrix and Crystal Material

Analysis of the NCC structures was carried out for a range of geometric parameters in order to determine optimal performance characteristics and overall trends. The following simulation were conducted at a dopant concentration of approximately $10^{18}\,\mathrm{cm}^{-3}$ and at a temperature of 300K with a difference of 10K in the transport direction.

The selection of the crystal material and matrix material of the NCC was analyzed by simulating a range of device lengths while maintaining the crystal spacing and crystal diameter proportional. Germanium was initially selected as the crystal material and silicon as the matrix material, followed by the transpose of materials. Figure 2 depicts the comparison of a homogeneous silicon, homogeneous germanium, silicon matrix germanium crystal (Si/Ge/Si), and germanium matrix silicon crystal (Ge/Si/Ge) devices. It should be noted from visual inspection of these devices that depending on the location of the strained conduction band edge, a cubic geometry energy barrier or well is formed due to the two dimensional nature of the crystal.

It is noted from Figure 2, that Si/Ge/Si device has the greatest Seebeck coefficient over other devices. This can be attributed to the increased barrier height of strained germanium crystal. These straining effects come from the difference in lattice constants between silicon and germanium crystalline lattice [9]. The strain shift the conduction band edge of the crystal. The germanium(crystal) barrier sees a increase of energy 3.75 times relative to unstrained germanium conduction band edge. The maximum in the trend of Seebeck can be attributed to a critical tunneling diameter for the crystal and critical size of the matrix material to transport around the crystal. This will be discussed when crystal size and spacing is analyzed.

In Figure 3, Ge/Si/Ge has the highest electrical conductivity followed by a homogeneous Ge device. The reason for the greater conductivity in Ge/Si/Ge is due to the straining of the silicon crystal. The silicon crystal is strained to the point that it becomes degenerate and the conduction band edge lies below the Fermi level. The straining of the crystal results in the silicon crystal seeing a decrease of 2.4 times the unstrained silicon conduction band energy. The following report will focus on analyzing the Si/Ge/Si due to it's optimal Seebeck performance.

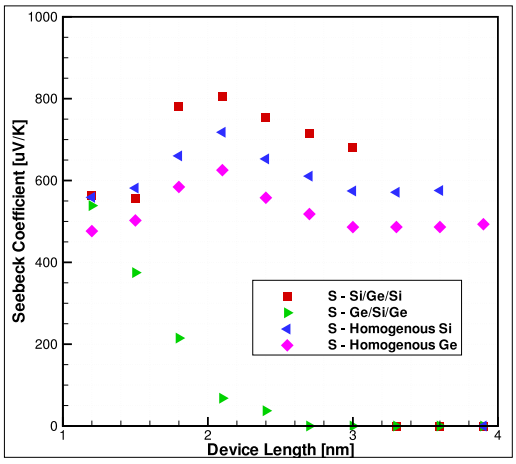

Figure 2. Seebeck coefficient for increasing device length, crystal spacing and crystal diameter increased proportionally. Device length is the transverse length from source to drain contacts.

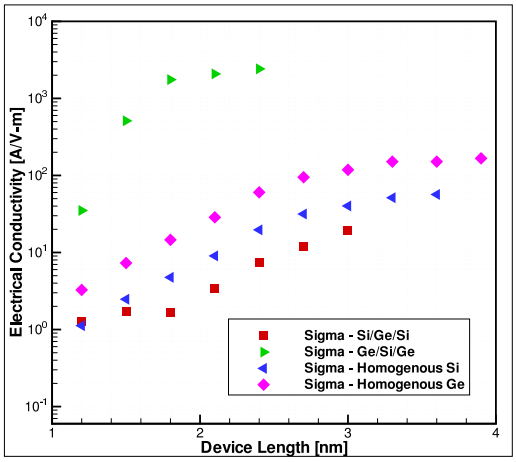

Figure 3. Electrical conductivity for increasing device length, crystal spacing and crystal diameter increased proportionally. Device length is the transverse length from source to drain contacts.

0.4 Effects of Crystal Spacing

As noted above, the periodic spacing of the crystals located within the matrix material is a design variable. When describing the crystal spacing in the context of this analysis, the distance from the edge of the crystal to the next nearest neighboring crystal edge(simulated with boundary condition) is twice the distance from the domain edge to the crystal edge Figure 1. This approximation for modeling the actual structure holds true for the transverse direction, but is only a first approximation of the longitudinal direction due to the transport profile that may arise from consecutive unit cells.

Constraining the crystal diameter (Lw) and varying the crystal spacing, Figure 4 describes the corresponding spacing trends.

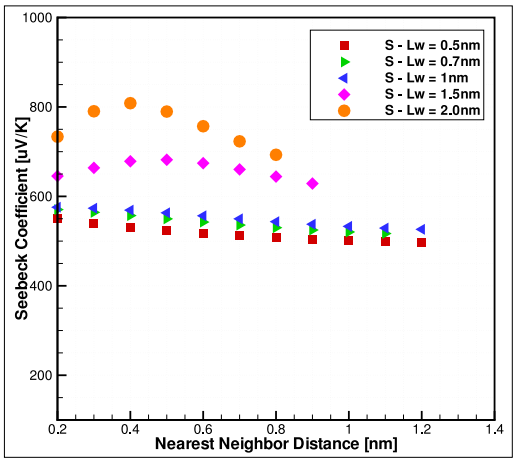

Figure 4. Seebeck coefficient for increasing crystal spacing, crystal diameter(Lw) held constant. Nearest Neighbor Distance is the distance from the crystal edge to the next crystal edge of a neighboring cell.

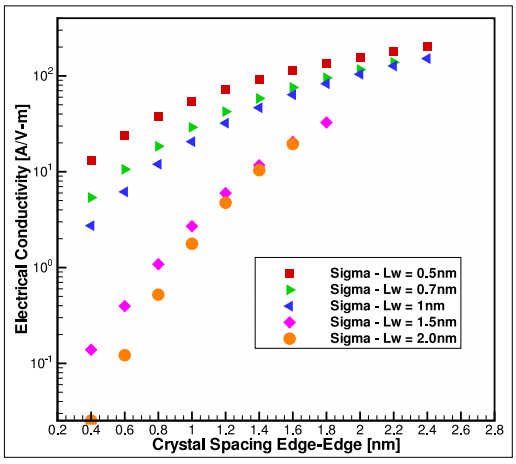

Figure 5. Electrical conductivity for increasing crystal spacing, crystal diameter(Lw) held constant. Distance is the distance from the crystal edge to the next crystal edge of a neighboring cell.

An extrema in the Seebeck coefficient exists for devices with larger crystal diameter(Lw). For the 2nm crystal device, the optimal Seebeck coefficient lies where the crystal spacing is half the crystal diameter. It is approximately the same for the 1.5nm device, in which a maximum lies near 0.7nm . These extrema can be attributed to a critical distance from the neighboring crystal in which the conduction bands of the silicon and germanium align leading to greater transport.

Figure 5 depicts the electrical conductivity becoming independent of the crystal spacing as it increases. If the crystal spacing is increased further, the electrical conductivity will continue to increase as more levels are lowered. For very large devices, the the conductivity will asymptotically approach a constant value related to that of the bulk material. The present simulation is entirely ballistic, however, so the value will actually be larger than that of the the bulk material. As the spacing between crystals increases, the transport of electrons through the crystal is no longer critical and electrons can remain in the silicon matrix material and transport around the crystal.

0.5 Effects of Crystal Diameter

To study the relationship of crystal diameter on the electrical transport, the crystal spacing(Lb) is held constant and the crystal diameter is varied for a range of values. In the case for the Si/Ge/Si structure the silicon matrix material is held constant and the germanium crystal is increased. Figure 6 suggests that crystal size is only slightly motivated to increase for larger crystal diameters. However, Figure 7 suggests that increased crystal size lowers the electrical conductivity significantly. In all, this suggests that the crystal diameter should be selected at a diameter as small as possible. The desire to have a small crystal stems from the increased probability to tunnel across the high strained

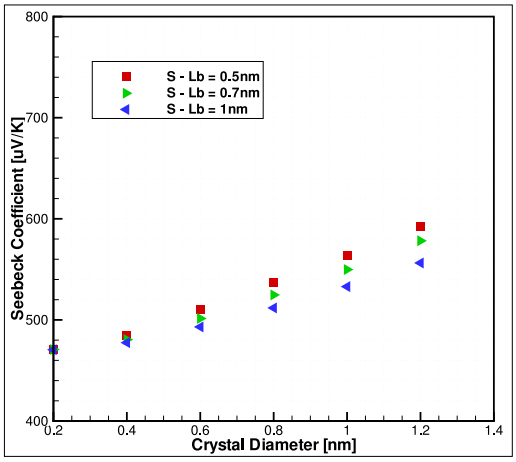

Figure 6. Seebeck coefficient for increasing crystal diameter, crystal spacing(Lb) held constant. Crystal diameter is cross-sectional diameter of the crystal.

barrier germanium crystals. Likewise, the effective area to transport at a lower unstrained silicon energy level is greater when the crystal cross-sectional area is small.

0.6 Thermoelectric Application

The following common metric is used to quantify the efficiency of thermoelectric devices:

$$ZT = \frac{S^2 \sigma T}{k} \quad (1)$$

The numerator of this figure of merit is a result of strictly the electrical properties, commonly referred to as the power factor.

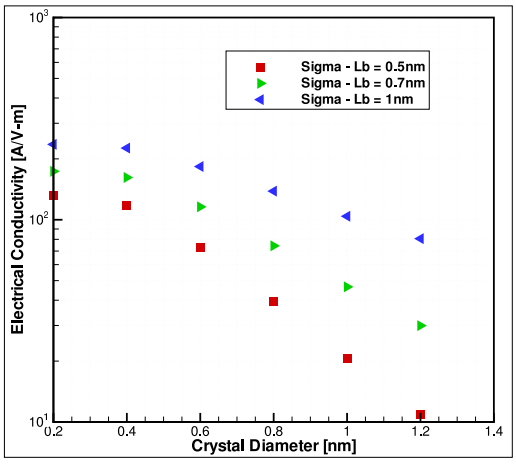

Figure 7. Electrical conductivity for increasing crystal diameter, crystal spacing(Lb) held constant. Crystal diameter is cross-sectional diameter of the crystal.

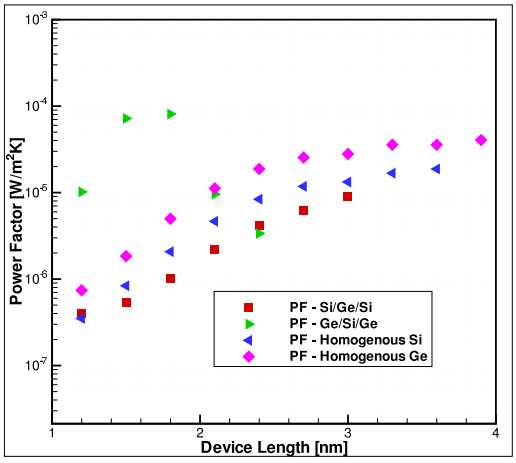

Figure 8. Power Factor for increasing device length, crystal spacing and crystal diameter increased proportionally. Device length is the transverse length from source to drain contacts.

Using the values obtained in Figure 2 and Figure 3 above, Figure 8 can be constructed, in which the crystal spacing and crystal diameter are varied proportionally. The figure suggests that the Si/Ge/Si NCC device is only marginally less efficient than the homogeneous silicon power factor. However, the Ge/Si/Ge device performs much better than its bulk constituents. These results provide guidelines for materials selection in NCC for thermoelectric performance.

CONCLUSIONS

This research constructed and implemented a computation NEGF method to solve the quantum equation for the I-V characteristic of nanocrystalline composite thermoelectric devices. Due to the two dimensional nature of NCC devices, quantum effects such as confinement, tunneling and alignment of density of state were observed for Nanocrystalline Composites. It was determined that the Si/Ge/Si constructed devices have the greatest Seebeck coefficient of all the structures studied. Furthermore, it was determined that a crystal diameter should be selected that is approximately half the size of the crystal neighboring spacing or as small as possible. Many of the trends observed in this research confirm the nature of single barrier type structures with the effects of tunneling, confinement and band shifting. This research has shown that NCC's have enhanced electrical properties which governs the numerator of the figure of merit. Additionally, research by others have suggested enhanced thermal properties(denomenator of figure of merit) for NCC. Overall this suggests greater than unity figures of merit, giving rise to the potential of NCC as good thermoelectric direct energy conversion devices.

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