Xanthippi Zianni*, Patrice Chantrenne and Dario Narducci

A Monte Carlo Study on the Effect of Energy Barriers on the Thermoelectric Properties of Si

DOI 10.1515/ehs-2016-0011

Abstract: Energy filtering by energy barriers has been proposed to interpret observations on large thermoelectric power factor (TPF) enhancement in highly doped nanocrystalline Si (nc-Si). Previous Boltzmann transport equation (BTE) modeling indicated that high TPFs could be explained as the result of the presence of energy barriers at the grain boundaries, the high Fermi energy due to the high doping level, and the formation of a low thermal conductivity second phase. To test the assumptions of the BTE modeling and provide more realistic simulations, we have performed Monte Carlo (MC) simulations on the transport properties of composite nc-Si structures. Here, we report on (i) the effect of an energy barrier, and (ii) the effect of multiple barriers on the conductivity and the Seebeck coefficient. In short structures, a TPF enhancement was found and it has been attributed to energy filtering by the energy barrier. The MC indicated that the TE performance can be improved by multiple barriers in close separation. It has been shown that TPF enhancement is possible even when the condition for thermal conductivity non-uniformity across the composite structure is not-fulfilled.

Keywords: thermoelectric efficiency, Silicon, energy filtering, energy barriers, Monte Carlo

Introduction

Efficient thermoelectric (TE) energy conversion requires high electrical conductivity σ, high Seebeck coefficient S, and low thermal conductivity κ. A measure of the TE efficiency of a material is the figure of merit Z that is expressed as the ratio of the thermoelectric power factor (TPF), σS^2, over the thermal conductivity: $Z = \sigma S^2/\kappa$. The TE efficiency of Si is low because of its high thermal conductivity. One way to reduce the thermal conductivity of Si is to use nanocrystalline Si (nc-Si) that has lower thermal conductivity than bulk Si because of enhanced phonon scattering on grain boundaries and imperfections. The additional scattering mechanisms in nc-Si, also scatter electrons and the electrical conductivity also decreases. The decrease of the thermal conductivity may, however, be more significant than the decrease of the electrical conductivity because phonons have larger mean free paths than electrons. For this, an overall Z enhancement is possible. Furthermore, in nc-Si the decrease of the electron conductivity is not the only effect of the structure inhomogeneity on the electron transport properties. Additional effects take place due to electrical potentials from inhomogeneous doping concentration, charge trapping at grain boundaries, imperfections etc. The modified electron TE transport properties may contribute themselves to the Z enhancement. Indeed, enhanced thermoelectric power factor (TPF) was measured in heavily doped Si in the presence of dopant segregation (Cojocaru-Miredin et al. 2013; Yusufu et al. 2014; Narducci et al. 2010, 2012, 2014; Narducci, Frabboni, and Zianni 2015). A remarkable five-fold TPF enhancement was observed in highly B-doped nanocrystalline Si films annealed at 1,000 °C and resulted from a non-conventional concurrent increase of the conductivity and the Seebeck coefficient (Narducci et al. 2010, 2012, 2014; Narducci, Frabboni, and Zianni 2015).

Energy filtering by energy barriers has been proposed to interpret the enhanced TE properties of highly doped Si (Narducci, Frabboni, and Zianni 2015). Energy filtering causes a decrease of the density of carriers participating in transport and consequently a decrease of the electrical conductivity. Filtered carriers have however higher energies, so that the Seebeck coefficient is enhanced. An overall increase of the TPF is then possible if the Seebeck coefficient enhancement compensates for the decrease of the conductivity. Much theoretical investigation has been devoted to the prospects for TPF enhancement by energy filtering using both simple and sophisticated models (Kim and Lundstrom 2011; Popescu et al. 2009; Neophytou et al. 2013; Kajikawa, 2012, 2013a, 2013b; Kim and Lundstrom 2012; Neophytou

***Corresponding author: Xanthippi Zianni,** Department of Aircraft Technology, Technological Educational Inst. of Sterea Ellada, 34400 Psachna, Greece, E-mail: xzianni@teiste.gr
Patrice Chantrenne, Universite de Lyon, INSA de Lyon, MATEIS UMR CNRS 5510, Villeurbanne 69621, France
Dario Narducci, Department of Materials Science, University of Milano Bicocca, via R. Cozzi 55, I-20125 Milano, Italy

and Kosina 2013). The ineffectiveness of the sole energy barriers to enhance thermoelectric efficiency has been proved in the literature (Bachmann, Czerner, and Heiliger 2012). A Boltzmann transport equation (BTE) model was presented (Neophytou et al. 2013) to interpret the large TPF enhancement observed in highly boron-doped nc-Si. It confirmed that the observed fivefold improvement of the TPF cannot be interpreted solely by invoking electrostatic energy barriers at grain boundaries. High TPFs could be explained as the result of three factors, namely the presence of energy barriers at the grain boundaries due to the formation of a second-phase originating by boron segregation, the high Fermi energy due to the high doping level, and a modification of the temperature variation profile due to the formation of a low-κ second phase.

Based on the BTE formalism, a parametric model has also been derived for the electron transport properties in the presence of an energy barrier (Zianni and Narducci 2015). The dependence of the σ and S on the Fermi energy, the height of the energy barrier and the type of dominant scattering mechanisms were explicitly indicated. It has also been explored the effect of the occurrence of two phases and of multiple barriers in real samples assuming a 1d-sequence of two types of resistors: (a) bulk-like and (b) barrier-like. It was predicted that an overall TE power factor enhancement could be possible in samples with significant density of energy barriers, grain widths smaller than ~50 nm and thermal conductivity of the barrier phase lower than that of the bulk-like phase.

The modeling within BTE formalism and the resistor network analysis pointed out the importance of the microstructure details and of the connectivity between the two phases. In order to quantitatively interpret measurements in real samples and to explore prospects for optimized structures, a more realistic modeling would be required. It would be necessary to take into account that the structures are composed by non-uniform distributions of nanograins and grain boundaries. For this we have performed kinetic Monte Carlo (MC) simulations on the electron transport properties of composite nc-Si structures. Here, we report on (i) the effect of an energy barrier, and (ii) the effect of multiple barriers on the conductivity and the Seebeck coefficient. To account for the effect of energy barriers, a 1d non-uniform doping profile has been assumed. Thin regions of low doping concentration have been assumed along the structure between Si regions with a higher doping concentration. The low-doping regions impose energy barriers to the carriers. The potentials in the material are calculated self-consistently during the simulation. In the BTE modeling of the composite material, the bulk Fermi level was used and an approximate resistor network model was assumed for the connectivity between the barrier phase and the bulk-like phase. The MC simulations were free of these assumptions. The Fermi level is extracted from the simulations taking into account the energy distribution of carriers and the Pauli's exclusion principle. The transport coefficients have been calculated from the currents through the composite structure. We present and discuss our results for (i) a single barrier and (ii) multiple barriers in Section "Method and Results". The conclusions are drawn in the final section.

Method and Results

Simulation Method

We have performed ensemble MC simulations on the electron transport properties. The MC technique is described in detail in standard references (e. g. Jacoboni and Reggiani 1983) and it is summarized here.

The mobile charge of the structure is represented by a number of "super-particles". The charge on each super-particle is $Q = eN/N_{sim,}$ where e is the elementary charge, N is the total number of mobile charges and N_{sim} is the number of super-particles used in the simulation. We used 10^4 super-particles that were adequate for ~5 % uncertainty on the transport coefficients of the investigated structures. The initial carrier concentration was determined by a preliminary solution of the POISSON equation for the actual doping configuration of the structure using COMSOL. After each simulation step, the actual carrier concentration was used to solve Poisson equation and update the potential profile across the structure. In the MC, the particles are initialized assuming thermal energy distributions with randomly oriented momenta. The carrier drifts under the influence of the electric fields during the free flight time. Then, a random number between 0 and 1 is drawn and it is compared with cumulative probabilities of scattering. A scattering mechanism is selected proportionally to the scattering probability of each process. The particle's state after scattering is stochastically chosen taking into account both energy and momentum conservation. The procedure is repeated for all particles. Ensemble averages are updated every time step. The super-particles are sampled at regular time-intervals until the required statistical accuracy is reached or the total simulation time ends.

The currents in the presence of external fields are directly provided by the MC. The transport coefficients are thereby calculated.

The electron energy bands are modelled analytically including non-parabolicity. The six ellipsoidal, energetically equivalent conduction band valleys of silicon are explicitly included. The phonon dispersion branches, acoustic and optical, are treated with the isotropic approximation. The parameters have been chosen to fit the bulk Si phonon dispersion curves for all phonon modes. The scattering rates have been calculated within Born approximation. Intravalley and intervalley electron transitions are included. The carrier transitions are induced by scattering by phonons, impurities, and other electrons. Electron-phonon interaction by deformation potential is assumed for both acoustic and optical phonons. Ionized impurities scattering is included. The effect of the electron-electron interactions has been taken into account in the determination of the electron distribution function. The Pauli's exclusion principle has been implemented using the rejection technique.

We have used our MC simulation code that allows for simulations of 1d, 2d and 3d structures. The Poisson equation is solved in 1d. We present results for n-doped Si with a doping concentration $10^{20}\,cm^{-3}$ and low doping barrier layers with n-doping of $10^{16}\,cm^{-3}$. The high carrier concentration ($10^{20}\,cm^{-3}$) was chosen so that the carriers are degenerate and have significant conductivity in bulk and also in the composite structure. The low doping concentration ($10^{16}\,cm^{-3}$) was chosen to provide adequately high energy barrier for energy filtering. The height of the energy barrier was obtained by the initial solution of the Poisson equation with COMSOL. It is ~60 meV for a 5 nm low doping region. We have used a 5 nm barrier that is appropriate for thermionic emission over the barrier in Si. For thinner barriers, we would have a contribution from carrier tunneling. For thicker barriers we would have contribution from diffusive transport. The results presented here have been produced with the 1d MC code that provides Poisson self-consistency. To test the 1d code, we compared it with the 3d code for uniform doping. Agreement was found in this case between the 1d code, the 3d code and the BTE.

The Effect of a Single Energy Barrier

Simulated transport properties of the composite structures are shown in Figure 1 for T = 100 K (red dots) and 300 K (blue squares) versus the structure length. The energy barrier is located in the middle of the structure and it is formed by a 5 nm Si layer with low doping. The potential energy profile is calculated self-consistently by solving the Poisson equation for charge redistributions during the simulations. In the present case, the barrier height was estimated to be ~60 meV. The corresponding bulk Si properties for the uniform material with electron concentration of $10^{20}\,cm^{-3}$ are also included in Figure 1 shown by stars.

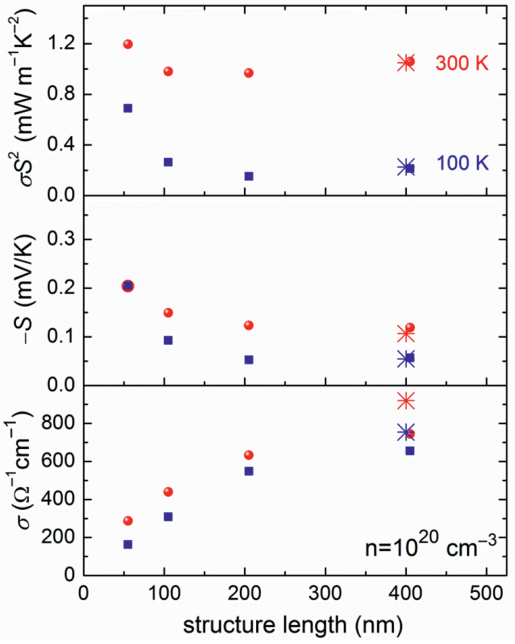

Figure 1: Simulated conductivity σ, Seebeck coefficient S and TPF σS^2 versus the structure length for T = 100 K (red dots) and 300 K (blue squares). The n-doping concentration is $10^{20}\,cm^{-3}$ in the bulk-like regions, and $10^{16}\,cm^{-3}$ in the 5 nm layer (barrier region) in the middle of the structure. Stars are for bulk Si with $10^{20}\,cm^{-3}$ electron concentration.

The conductivity σ is lower than in bulk Si for all structure lengths. This is because a smaller number of carriers participate to transport through the complex structure compared to bulk. Carriers with energies lower than the barrier energy are filtered out and do not contribute to transport. For the same barrier region, the conductivity decreases more significantly with decreasing structure length. This can be qualitatively understood if we see the structure as composed by two bulk-like grains separated by a short barrier-like grain. The barrier conductivity is smaller than the bulk conductivity and the overall conductivity is therefore smaller than in bulk. The energy barrier grain has a bigger contribution to the overall resistance in shorter structures. The decrease is, therefore, bigger in shorter structures.

For structure length smaller than ~200 nm, the Seebeck coefficient S is higher than in bulk Si. In longer structures the Seebeck coefficient was found to be

comparable to its bulk value. This is because in short structures the barrier phase dominates the effective S that is therefore higher than in bulk Si. In long structures, the bulk-like phase dominates the effective S that is equal to the bulk value. One should be therefore aware that the S enhancement by the energy barrier may be screened in a composite structure by the contribution of an extended bulk-like phase around the barrier phase.

The effective TPF σS^2, is determined by the two competing trends: the decrease of the conductivity and the increase of Seebeck. In structures with length smaller than ~200 nm, an overall TPF enhancement has been found compared to bulk. The enhancement reaches the factor ~3.8 at 100 K and ~1.2 at 300 K in the shortest structure 25 nm/5 nm/25 nm. These findings are consistent with our BTE calculations for the barrier-like phase (Zianni and Narducci 2015).

The Effect of Multiple Energy Barriers

We now consider the effect of multiple barriers. Schematics of the simulated structures are shown in Figure 2.

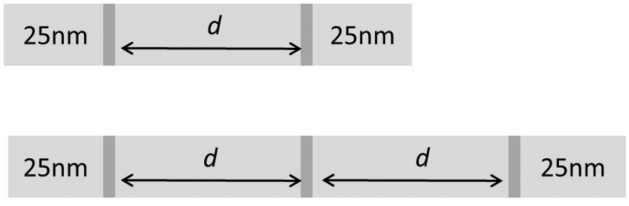

Figure 2: 1d-schematics of the composite structures with two barriers (upper panel) and with three barriers (lower panel). Here, d is the width of the grain separating subsequent barriers.

In Figure 3 the simulated coefficients of composite structures with two barriers (grey) and three barriers (light grey) is plotted versus the grain width d. The values for the reference single barrier structure 25 nm/5 nm/25 nm, that exhibits the highest TPF enhancement, are shown with red squares at 300 K and blue squares at 100 K. The bulk values for electron concentration $10^{20}\,\mathrm{cm}^{-3}$ are shown in stars.

The transport coefficients of the multiple barriers structures show the same characteristic dependence of the magnitudes of σ and S, in the presence of energy barriers, on the relative lengths of the bulk-like phase and the barrier phase and on the temperature, as the single barrier structures. The transport properties of the two- and three-barriers structures have been found in qualitative agreement at 300 K. Small deviations have been found at 100 K. This is because the effects of the barriers are shown at lower temperatures in more detail as transport over the barrier is a thermally activated process. At higher temperatures, more carriers have energies higher than the barrier height and participate to transport.

In Figure 3, it can be seen that at 100 K the conductivities of the three barriers structures are higher than those of the two barriers structures. This is because the bulk-like grains extend over longer length in the three barriers structures compared with the corresponding two barriers structures with same grain width. Therefore, the overall contribution of the bulk-like grains to the effective conductivity is bigger in the three barrier structures. Their conductivity is higher than that of the corresponding two barriers structures. In Figure 3, it can be also noticed that the conductivities of the three barriers structures are nearly the same as those of the two barriers structures. This is because the effect of the barriers on the conductivity becomes weaker with increasing thermal energy, since more carriers have higher energies than the barrier energy and participate to transport. The Seebeck coefficient also has been found higher in the three barriers structures. A cross-over behavior can be noticed in the transition from wide- to short-grain widths in this case. The higher Seebeck coefficient in the three barriers structures compared to the two barriers structures is due to more efficient energy filtering in the presence of multiple barriers. Transport is diffusive within the grains when they are not very small. As the grain size decreases, transport becomes more ballistic. The crossover between diffusive and ballistic transport differs quantitatively for the three barriers and the two barriers structures. This effect leads to the Seebeck coefficient being higher for the double barrier for grain lengths between 50 and 150 nm. Energy filtering of the more energetic carriers occurs more efficiently by three barriers than by two barriers. The decrease of the conductivity and the increase of Seebeck coefficient are maximized in the structures with the shortest grains of width 25 nm. These structures show the maximum TE power factor enhancement: by a factor of 4.5 in the two-barrier structure and by a factor of 6 in the three-barrier structure. The TPF enhancement is lower at 300 K because energy filtering is less efficient at higher temperatures as more carriers have energies higher that the energy barrier and participate to transport. Higher energy barriers would be required at 300 K for more efficient energy filtering and bigger TPF enhancement. In our simulations, energy barriers were

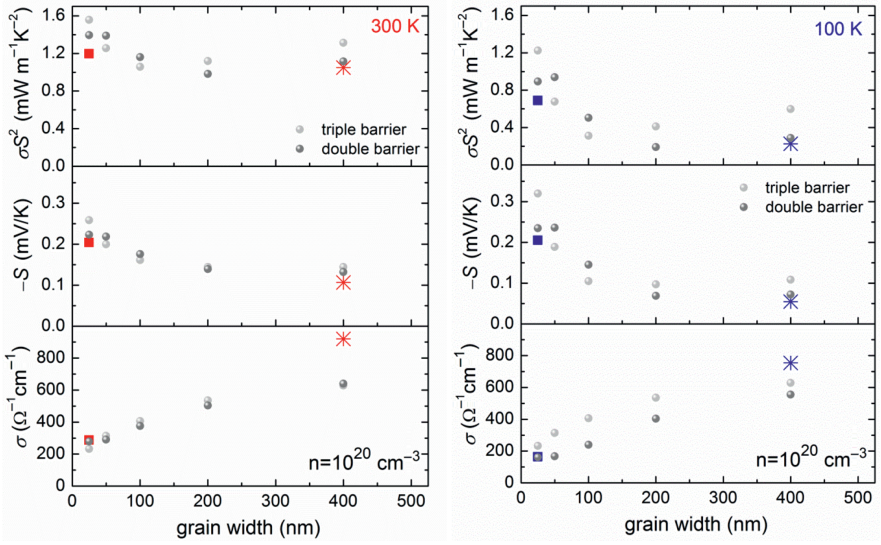

Figure 3: Simulated conductivity σ, Seebeck coefficient S and TPF σS^2 versus the grain width in composite structures with two barriers (black dots) and three barriers (grey dots) barriers for T = 300 K (left panel) and 100 K (right panel). The doping concentrations are as in.

formed by non-uniform doping. Additional sources of energy barriers and higher barriers are expected at grain boundaries in highly doped samples due to dopant segregates and trapped charges.

Conclusions

We have explored the effect of energy barriers in the TE transport coefficients and TPF of nc-Si using the Monte Carlo technique. The composite nc-Si structure was simulated by a 1d-sequence of bulk-like grains separated by thin barrier regions. The MC results clearly showed the decreased σ and the enhanced S in the single barrier structure in agreement with our previous BTE calculations. In short structures, a TPF enhancement was found. It has been attributed to energy filtering by the energy barrier. The MC simulations showed that the effect of the energy barrier in the composite structure is a thermally activated process. This justifies the corresponding assumption in our previous BTE modeling. The MC indicated that the TE performance can be improved by multiple barriers in close separation. It has been shown that when the barrier separation increases, the barrier phase contribution decreases, and the bulk-like phase becomes increasingly important. The competition of the two phases, the barrier-like and the bulk-like has been clearly shown in our MC simulations.

Finally, we comment on the condition for thermal conductivity non-uniformity set as one of the requirements for observation of TPF enhancement, based on the BTE modeling. The MC simulations showed that TPF enhancement is possible even without this condition. Thermal conductivity uniformity was assumed in the MC simulations. Nevertheless, TPF enhancement was found in structures with small grain width. It should be noted that the MC modeling was free of any assumptions on the transport regime throughout the composite structure whereas diffusive transport was assumed in the grains in the BTE modeling. This further indicates that the MC technique can provide physics insight and reliable estimations on the thermoelectric properties of composite structures.

References

Bachmann, M., M. Czerner, and C. Heiliger. 2012. "Ineffectiveness of Energy Filtering at Grain Boundaries for Thermoelectric Materials." Physical Review B: Condensed Matter and Materials Physics 86:115320.

Cojocaru-Miredin, O., F. Cristiano, P.-F. Fazzini, D. Mangelinck, and D. Blavette. 2013. "Extended Defects and Precipitation in Heavily B-Doped Silicon." Thin Solid Films 534:62.

Jacoboni, C., and L. Reggiani. 1983. "The Monte Carlo Method for the Solution of Charge Transport in Semiconductors with Applications to Covalent Materials." Reviews of Modern Physics 55:645.

Kajikawa, Y. 2012. "Conduction Model Covering Non-Degenerate Through Degenerate Polycrystalline Semiconductors with Non-Uniform Grain-Boundary Potential Heights Based on an Energy Filtering Model." Journal of Applied Physics 112:123713.

Kajikawa, Y. 2013a. "Effects of Potential Barrier Height and Its Fluctuations at Grain Boundaries on Thermoelectric Properties

of Polycrystalline Semiconductors." Journal of Applied Physics 114:053707.

Kajikawa, Y. 2013b. "Effects of Grain-Boundary Potential Barrier Height and Its Fluctuation on Conductivity of Polycrystalline Semiconductors in the Ionized-Impurity-Scattering Dominated Case." Journal of Applied Physics 114:043719.

Kim, R., and M. S. Lundstrom. 2011. "Computational Study of the Seebeck Coefficient of One-Dimensional Composite Nano-Structures." Journal of Applied Physics 110:034511.

Kim, R., and M. S. Lundstrom. 2012. "Computational Study of Energy Filtering Effects in One-Dimensional Composite Nano-Structures." Journal of Applied Physics 111:024508.

Narducci, D., S. Frabboni, and X. Zianni. 2015. "Silicon De Novo: Energy Filtering and Enhanced Thermoelectric Performances of Nanocrystalline Silicon and Silicon Alloys." Journal of Materials Chemistry C 3:12176.

Narducci, D., B. Lorenzi, X. Zianni, N. Neophytou, S. Frabboni, G. C. Gazzadi, A. Roncaglia, and F. Suriano. 2014. "Enhancement of the Power Factor in Two-Phase Silicon-Boron Nanocrystalline Alloys." Physica Status Solidi A 211:1255.

Narducci, D., E. Selezneva, G. Cerofolini, S. Frabboni, and G. Ottaviani. 2012. "Impact of energy filtering and carrier localization on the thermoelectric properties of granular semiconductors." Journal of Solid State Chemistry 193:19.

Narducci, D., E. Selezneva, G. Cerofolini, E. Romano, R. Tonini, and G. Ottaviani. 2010. "Opportunities and Challenges in the Use of Heavily Doped Polycrystalline Silicon as a Thermoelectric Material. An Experiment Study." 8th European Conf. on Thermoelectrics, p. 141.

Neophytou, N., and H. Kosina. 2013. "Optimizing Thermoelectric Power Factor By Means Of a Potential Barrier." Journal of Applied Physics 114:044315.

Neophytou, N., X. Zianni, H. Kosina, S. Frabboni, B. Lorenzi, and D. Narducci. 2013. "Simultaneous Increase in Electrical Conductivity and Seebeck Coefficient in Highly Boron-Doped Nanocrystalline Si." Nanotechnology 24:205402.

Popescu, A., L. M. Woods, J. Martin, and G. S. Nolas. 2009. "Model of Transport Properties of Thermoelectric Nanocomposite Materials." Physical Review B: Condensed Matter and Materials Physics 79:205302.

Yusufu, A., K. Kurosaki, Y. Miyazaki, M. Ishimaru, A. Kosuga, Y. Ohishi, H. Muta, and S. Yamanaka. 2014. "Bottom-up Nanostructured Bulk Silicon: A Practical High-Efficiency Thermoelectric Material." Nanoscale 6:13921.

Zianni, X., and D. Narducci. 2015. "Parametric Modeling of Energy Filtering by Energy Barriers in Thermoelectric Nanocomposites." Journal of Applied Physics 117:035102.