Thermoelectric power factor optimization in nanocomposites by energy filtering using NEGF

Mischa Thesberg, Mahdi Pourfath
and Hans Kosina
Institute for Microelectronics
TU Wien
Vienna, Austria

Neophytos Neophytou
University of Warwick
Coventry, U.K.

I. Introduction

The thermoelectric (TE) performance of materials is determined by the figure of merit $ZT = \sigma S^2 T/\kappa$, where σ denotes the electrical conductivity, S the Seebeck coefficient and κ the thermal conductivity. Large improvements in ZT have recently been reported in nanoscale materials due to drastic reduction in κ[1]. On the other hand, much less success has been achieved in improving the power factor (σS^2), and ZT still remains low. Energy filtering in nanocomposite materials with embedded potential barriers is a promising way to improve σS^2 via improvements in the Seebeck coefficient [2], [3]. Indeed, the improvement in the Seebeck coefficient of nanometers-size layer superlattices has been demonstrated in several experimental works. Significant benefits to the overall power factor, however, were never observed in these structures due to large reductions in σ. In this work, we use the Non-Equilibrium Greens Function (NEGF) method to illustrate the design details under which improvements in σS^2 can be achieved by energy filtering. We further demonstrate that variation of the design parameters, and most importantly in the barrier heights is a strong detrimental mechanism which can take away most of the energy filtering benefits.

II. The NEGF Method

In this section the specific of the NEGF method will be outlined. The central object in this theory is the Green's function:

$$G(E) = [E - H(E) - \Sigma_c(E) - \Sigma_{sc}(E')]^{-1} \tag{1}$$

where $H(E)$ is the system Hamiltonian and Σ_c/Σ_{sc} represent perturbations to the Hamiltonian that account for the effects of the contacts and scattering respectively and are called "self-energies". If these self-energies were to be calculated explicitly the result would essentially be a non-equilibrium perturbative theory, accurate only to first order. However, as we will see, the self-energies are determined self-consistently which amounts to an infinite order expansion, though only in Feynman diagrams of first-order. Effectively this means that NEGF represents an infinite-order perturbation theory, but only in one-scatter processes (i.e. multi-scatter processes are neglected as are all non-perturbative phenomena). Related to the Green's functions, the"correlation functions" are defined as:

$$G^{n/p} = G\Sigma^{in/out}G^\dagger \tag{2}$$

where $\Sigma^{in/out}$ are simply called the in or out scattering functions. The in/out scattering functions are a sum of the individual in/out scattering functions for each contact and for scattering (one for each self-energy in the Green's function). The contact in/out functions have a simple form:

$$\Sigma_c^{in}(E) = if(E)(\Sigma_c(E) - \Sigma_c^\dagger(E)) \tag{3}$$

$$\Sigma_c^{out}(E) = i(1-f(E))(\Sigma_c(E) - \Sigma_c^\dagger(E)) \tag{4}$$

where $f(E)$ is the Fermi-Dirac distribution. However, the expression for the scattering functions is far more complex[4]:

$$\Sigma_{sc}^{in/out}(E) = \int_0^\infty \Big(D^{em}(\hbar\omega)G^{n/p}(E+\hbar\omega) + D^{ab}(\hbar\omega)G^{n/p}(E-\hbar\omega)\Big)\frac{dE}{2\pi} \tag{5}$$

where $D^{em/ab}$ are the emission and absorption constants. The reason these constants are called such will be made clear later.

Within the NEGF formalism the Green's function contains information about the available states of the system, theirS number and energy. This is evidenced by the fact that the diagonal elements of the Green's

function can be shown to be proportional to the density of states. While the Green's function holds information about the possible states of the system, the correlation function holds comparable information about their occupancy which is suggested by its dependence on both the Green's function (which holds state information) and the Fermi-Dirac function (which dictates fermionic occupancy). To wit its diagonal elements are proportional to the occupancy probabilities or charge density.

Without contacts or scattering (i.e. at zero self-energy) the Green's function must be solved for all energies. In very simple cases this can be done analytically, however, for all others it must be done computationally by evaluating it at many points along a grid of energy points extending from some minimal energy to some maximum. As the occupancy of states far from the Fermi level are either 0 or 1 these limits need not extend far from the Fermi level. Thus, if there are N energy points considered about the Fermi level then the inversion must be done N times producing either N Green's functions (if the inversion could be done analytically) or N Green's matrices whose size is that of the Hamiltonian (if done numerically). From these Green's functions, quantities like the density of states, the state occupancy, charge density and current can be determined.

When contacts are considered the formalism is only slightly modified, provided one has a clear expression for the contact self-energies. The determination of these expressions can be very complex but is an issue ignored here. The main difficulty in NEGF simulation is the treatment of scattering.

The correlation functions are dependent on the in and out scattering functions ($\Sigma^{in/out}$). The in and out scattering functions at an energy E are dependent on the correlation functions at an energy $E \pm \hbar\omega$. Thus there is a circular dependence and the numerical task amounts to determining the scattering function for which the two quantities (the correlation function and the scattering functions) are self-consistent. However, in the most general case $D^{em/ab}$ must be assumed to be non-zero for all values of $\hbar\omega$ within an allowed phonon band. In this case one has an enormously complex self-consistency problem with all energies being completely dependent on all other energies. Although in principal such a problem is tractable, such calculations are almost never done. Rather assumptions are made about the form of $D^{em/ab}$ that greatly simplify the calculation. Specifically, for acoustic phonons one assumes that scattering is elastic and only momentum and not energy is exchanged by electron-phonon interactions. In such a case $D^{em/ab}$ can

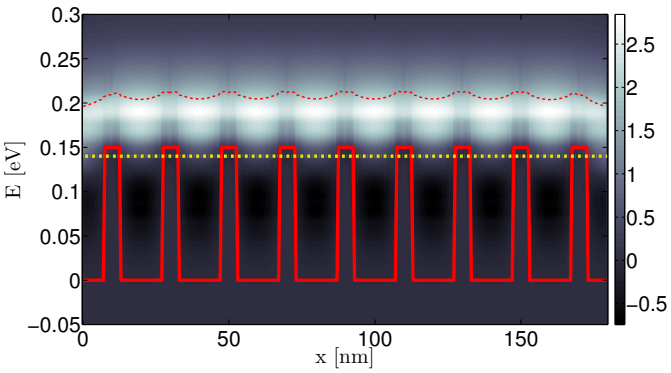

Fig. 1. Sample data for a nanocomposite channel. The current density versus position (colormap). Superimposed on the image are the potential barriers and the carriers energy expectation value $\langle E \rangle$.

be considered to be Dirac delta functions centered at zero and only $\hbar\omega = 0$ is considered and the integration is dropped. In this case self-consistency can be determined at each energy entirely independent of one another. The case for optical phonons is even more complex.

It is common practice to assume that optical phonons in NEGF have a completely flat band profile (i.e. their dispersion is $\omega(k) = \hbar\omega_0$ or independent of momentum). Under this approximation $D^{em/ab}$ are Dirac delta functions centered at $\pm\hbar\omega$ and although each energy is no longer independent they depend only on two other energies; one at $E + \hbar\omega$ representing the case where an electron is being added to energy E from $E - \hbar\omega$ by emitting a phonon of energy $\hbar\omega$ and thus losing that energy (which is why D^{em} is so named) and the converse case of absorption allowing an electron initially at $E - \hbar\omega$ to scatter into a state at energy E.

The limited interdependency of optical phonon scattering requires one to calculate and store the correlation functions for all energies, where in the independent energies case one could solve each energy one at a time. For large Hamiltonians (i.e. large systems) this can take a large amount of computer memory. In order to avoid this it is common practice to only consider the diagonal elements of the in and out scattering functions. If the Hamiltonian is in a position space basis then this means that scattering can only occur from $r \rightarrow r'$ if $r = r'$, which is to say that scattering is assumed to only occur locally. The validity of this approximation has been justified in many cases[4], [5] but its appropriateness must be considered with each new system. In systems where non-local scattering is an important effect (such as with polar optical phonons, for example) one must keep the entire set of matrices and thus confine themselves to

smaller systems.

The basic NEGF algorithm[4] for a system with acoustic and optical phonons in the local scattering approximation proceeds as follows:

1) Represent the system Hamiltonian in a convenient basis (often real-space or a hybrid of real-space in the transport direction, Fourier space in the transverse).
2) Determine the contact self-energies (Σ_c) for all N energies E and save them (contacts self-energies in a real space basis couple only to the ends of the device and thus are sparse matrices and the entire matrix can be stored).
3) Initially assume the scattering self-energies to be zero ($\Sigma_{sc} = 0$).
4) Calculate G from Σ_c and Σ_{sc}.
5) Calculate $\Sigma_c^{in/out}$ ($\Sigma_{sc}^{in/out}$ is calculated later but is taken to simply be zero on the first step) from the Fermi-Dirac functions and Σ_c and Σ_{sc}.
6) Calculate $G^{n/p}$ from $\Sigma_c^{in/out}$ and $\Sigma_{sc}^{in/out}$ for all energies. One only needs to keep the diagonal elements but one must store it for all energies.
7) With $G^{n/p}$ and $\hbar\omega_0$ (the optical phonon energy) calculate $\Sigma_{sc}^{in/out}$.
8) Calculate quantities of interest (i.e. current, charge density, density of states, etc.).
9) Check for convergence of self-consistency of $G^{n/p}$ and $\Sigma_{sc}^{in/out}$. If not converged go to 4.

There are a number of ways to determine whether self-consistency has been achieved. Commons choices are to save either the charge density or the current every time step 8 is reached and when a new value is calculated compare to the old and if the change is only within some set convergence criteria stop the loop.

Convergence, especially in the work done here where potential features are very sharp and scattering is intense, can often be an issue. There are a number of schemes to either speed (should it be slow) or improve the chances of (should it be unreliable) of convergence. The simplest way to improve the chance of convergence is to take the new $\Sigma_{sc}^{in/out}$ in times some quantity α and add it to $(1-\alpha)\Sigma_{sc}^{in/out}(old)$ which is the in scattering function from the previous step. Thus, for example, if $\alpha = 0.5$ then the new in scattering function is half the new and half the old. This weighting generally reduces divergence but also slows convergence and thus, as with all convergence tricks, should be considered on a case by case basis.

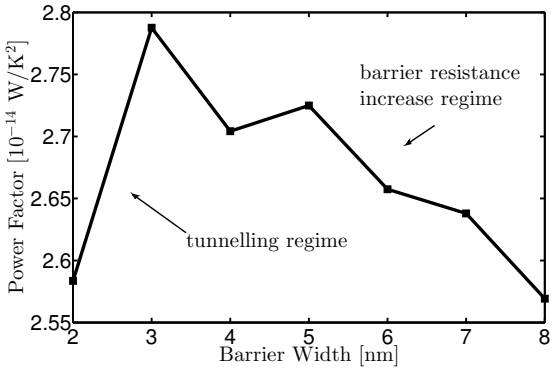

Fig. 2. Power factor versus barrier width. The optimal barrier width is ∼3 nm, which is thick enough to prevent tunnelling, but thin enough to keep the electrical resistance from barriers low.

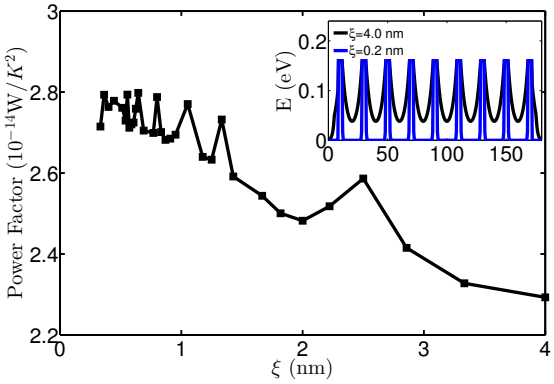

Fig. 3. Power factor versus barrier shape, defined as an exponentially decaying profile, described by a decay length, ξ, from the top of the barrier. The limit $\xi = 0$ corresponds to a square barrier (left side), which is found to be the optimal one.

III. Results and Discussion

We use the NEGF method in the effective mass approximation, including both acoustic and optical phonon scattering. Figure 1 illustrates the simulated 1D channel geometry. It shows the current spectrum and how it fluctuates in energy during emission / absorption of optical phonons. Also shown is the potential profile, Fermi level and average carrier energy. Previous works have indicated that under optimal conditions the transport in the wells needs to be semi-ballistic, where carriers only lose part of their energy before they reach the next barrier[6], [7]. In addition, it was also indicated that ideally the barrier height needs to extend $\sim k_B T$ above the Fermi level[6], [7]. Thus, in this work we calibrate the geometry, electron-phonon scattering, Fermi level, and barrier height for these optimal conditions.

Once this is done, we proceed by investigating the

performance of energy filtering processes under statistical fluctuations in the design parameters. The first parameter we examine is the width of the barrier W. Figure 2 shows the power factor versus W. We can observe that the barriers need to be thick enough to prevent tunneling (which is detrimental to S and could cause up to ∼40% degradation in performance), but thin enough for reduced resistivity (so ∼2-3nm), since the carrier energy and momentum can relax on top of the barriers and acquire reduced velocities. The next parameter we consider is the actual shape of the barrier. In practice, an ideal rectangular barrier would not be achievable, thus we examine the influence of deviations from the rectangular shape on the performance. Figure 3 shows that the rectangular barriers are ideal (left side), which shows that ∼30% improvement can be achieved compared to the bulk TE material case. As we deviate from that shape the power factor drops (approaching the bulk case right side). Finally, the last parameter we examine, is fluctuations in the height of the potential barriers V_B. The results are shown in Fig. 4 (black line). In this case, we vary the barrier heights along the transport path according to a Gaussian distribution. As the variation increases, a large drop is observed in the power factor (black line). We perform the same studies for variations in the barrier position (blue line) and the barrier width (red line), which introduce only small power factor reduction.

IV. Conclusion

Using the NEGF method we computed the thermoelectric power factor in nanocomposite channels in the presence of energy barriers. We show that ideally, power factor improvements up to 30% can be achieved using energy filtering under optimal conditions. However, we show that this is improvement is sensitive to structure imperfections. Fluctuations in the barrier width and well size do not affect performance significantly, but fluctuations in the barrier shape and most importantly the barrier height (even of the order of 5 meV) could take away most of the power factor improvements, and therefore, need to be avoided.

Acknowledgment

We acknowledge the Vienna Scientific Computing Cluster for computational resources and funding from the Austrian Science Fund FWF, project code P25368-N30.

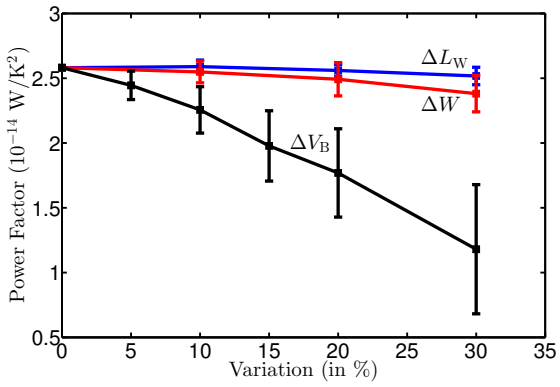

Fig. 4. Power factor (σS^2) versus statistical variation of the barrier placement (blue line), width (red line), and height (black line) along the transport path. It is clear that performance is most substantially degraded by barrier height variation.

References

[1] T. C. R. Venkatasubramanian, E. Siivola and B. O'Quinn, "Thin-film thermoelectric devices with high room-temperature figures of merit," *Nature*, vol. 413, pp. 597–602, 2001.

[2] D. Vashaee and A. Shakouri, "Improved thermoelectric power factor in metal-based superlattices," *Phys. Rev. Lett.*, vol. 92, p. 106103, Mar 2004. [Online]. Available: http://link.aps.org/doi/10.1103/PhysRevLett.92.106103

[3] N. Neophytou and H. Kosina, "Optimizing thermoelectric power factor by means of a potential barrier," *Journal of Applied Physics*, vol. 114, no. 4, pp. –, 2013. [Online]. Available: http://scitation.aip.org/content/aip/journal/jap/114/4/10.1063/1.4816792

[4] S. Koswatta, S. Hasan, M. Lundstrom, M. Anantram, and D. Nikonov, "Nonequilibrium green's function treatment of phonon scattering in carbon-nanotube transistors," *Electron Devices, IEEE Transactions on*, vol. 54, no. 9, pp. 2339–2351, Sept 2007.

[5] R. Rhyner and M. Luisier, "Phonon-limited low-field mobility in silicon: Quantum transport vs. linearized boltzmann transport equation," *Journal of Applied Physics*, vol. 114, no. 22, pp. –, 2013. [Online]. Available: http://scitation.aip.org/content/aip/journal/jap/114/22/10.1063/1.4845515

[6] R. Kim and M. S. Lundstrom, "Computational study of energy filtering effects in one-dimensional composite nano-structures," *Journal of Applied Physics*, vol. 111, no. 2, pp. –, 2012. [Online]. Available: http://scitation.aip.org/content/aip/journal/jap/111/2/10.1063/1.3678001

[7] N. Neophytou, X. Zianni, H. Kosina, S. Frabboni, B. Lorenzi, and D. Narducci, "Simultaneous increase in electrical conductivity and seebeck coefficient in highly boron-doped nanocrystalline si," *Nanotechnology*, vol. 24, no. 20, p. 205402, 2013. [Online]. Available: http://stacks.iop.org/0957-4484/24/i=20/a=205402