Simulation studies of nanostructured thermoelectric materials

N. Neophytou[1], S. Foster[1], V. Vargiamidis[1], D. Chakraborty[1], L. Oliveira[1], C. Kumarasinghe[1], and M. Thesberg[2]
[1]School of Engineering, University of Warwick, UK, email: n.neophytou@warwick.ac.uk
[2]Technical University of Vienna, TU Wien, Vienna, Austria

***Abstract*—** In this work we use modelling and simulation to investigate directions in achieving large thermoelectric figure of merit *ZT* in hierarchically nanostructured materials. To this end we explore both reduction of thermal conductivity and improvement of the power factor. We employ a series of models and computational techniques, from analytical models to fully quantum mechanical non-equilibrium Green's function simulations and to large scale Monte Carlo simulations. We show that nanostructuring across different length scales, which can drastically reduce the thermal conductivity of thermoelectric materials, can also be designed to retain, or even improve the power factor.

I. Introduction

Nanostructured materials have shown great potential to achieve extremely low thermal conductivities, and thus, improve thermoelectric performance. Hierarchical nanostructuring, where phonons of different wavelengths scatter on features of different sizes have resulted in $ZT > 2$ [1]. However, less attention has been paid to the possibility of designing nanostructured materials for improving the thermoelectric power factor (PF). Recent experimental and theoretical works by us and others, however, have indicated that nanostructuring can indeed provide additional improvements from the power factor [2-8]. For effective reduction in thermal conductivity and power factor improvements, advanced simulations, which can capture all essential transport physics and nanoscale geometry details, are needed.

In this work, we present our simulation efforts to address both electronic and phononic transport in nanostructured materials. With regards to electronic transport, we employ the fully quantum mechanical electron transport non-equilibrium Green's function method (NEGF) for two-dimensional nanocomposites of arbitrary geometries. We present simulations for thermoelectric power factor in materials with embedded nanoinclusions (NIs) and voids, and hierarchical geometries where nanoinclusions are placed within nanograins as shown in **Fig. 1**. The NEGF formalism captures all important effects that relate to the different and non-uniform geometrical features extending from a few to hundreds of nanometers. With enough computational power, electron-phonon interactions are also included, which allows treatment from fully coherent to incoherent, and from fully ballistic to diffusive transport regimes. With regards to phonon transport, we present our newly developed phonon Monte Carlo simulator and our simulation work on highly disordered nanostructured materials. Finally, we discuss our efforts to include insight from atomistic techniques (e.g. Density Functional Theory and Molecular Dynamics) into the simulators, allowing a more accurate treatment of electrothermal transport at the nanoscale.

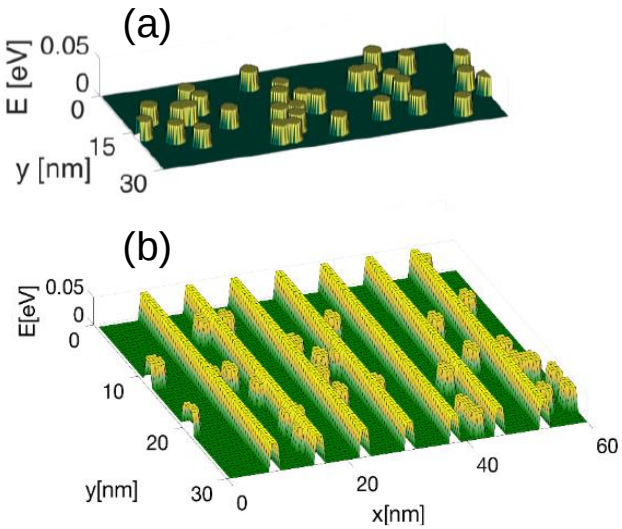

Fig. 1. (a) A schematic of a material geometry with embedded nanoinclusions of diameter d = 3 nm randomly placed in the material. (b) A hierarchically nanostructured material geometry, where nanoinclusions of 3 nm in diameter are embedded within a superlattice structure. Both the nanoinclusions and superlattice boundaries are treated as potential barriers for charge carriers with barrier height V_B.

II. Key Results

We first consider the influence of nanoinclusions alone on the power factor and for this investigation we employ the diffusive (incoherent) scattering regime. The thermoelectric power factors versus barrier height V_B are shown in **Fig. 2** for four simulated geometries as shown in the insets of Fig. 2. The four simulated geometries are: i) a 2×4 array of NIs (green lines), ii) a 4×4 array (black lines), iii) a 6×4 array (blue lines), and iv) an 8×4 array (red lines). The Fermi level is placed at E_F = 0.05 eV (dashed-red line in Fig. 2), i.e. we consider degenerate high carrier concentration conditions. Increasing density decreases the electrical conductance, but increases the Seebeck coefficient. The result is that the power factor increases from the pristine channel value by ~10% until the barrier height of the NIs reaches k_BT below the Fermi level, and for higher barrier heights it drops. This indicates that NIs provide some filtering of the low energy carriers, although its magnitude is lower compared to that of superlattices. The dashed lines extend the NI barrier height to infinity, resembling a void/porous structure. In that case the power factor saturates to a lower value compared to the pristine

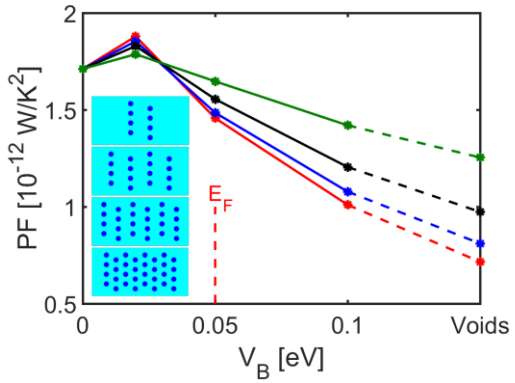

Fig. 2. The power factor in a material geometry with embedded nanoinclusions of increasing density as indicated in the insets. The position of the Fermi level is indicated by the dashed red line. The power factor is independent of the nanoinclusion density for low barrier heights V_B (below the Fermi level). The far right points indicate the power factor in structures with voids, i.e. V_B=inf. (Results adapted from Refs. [8] and [9])

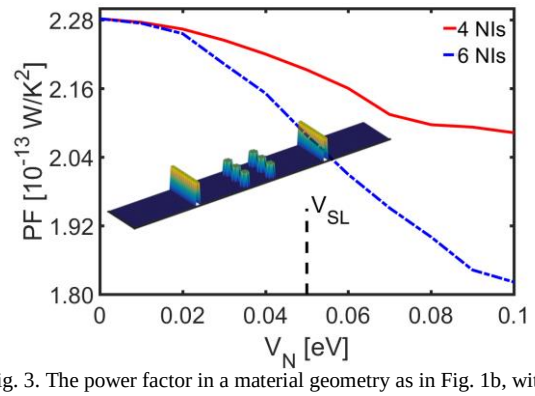

Fig. 3. The power factor in a material geometry as in Fig. 1b, with embedded nanoinclusions within a superlattice type structure (for simplicity only one superlattice period is simulated) vs the nanoinclusion barrier height V_N. The superlattice barrier height is indicated by the dashed line. The results for two different nanoinclusion densities are shown.

structure. However, the important point to stress here is that the influence of the NI density is not significant on the power factor when their barrier heights are low compared to the Fermi level. Thus, high NI densities can be employed to maximize the reduction in thermal conductivity without degrading the power factor, and even resulting in a small positive effect.

Next, we perform simulations for the power factor in geometries that include superlattice-type barriers and NIs, as shown in Fig. 1b. For simplicity we only consider one superlattice period and examine two different NI densities for varying barrier height values. For this simulation we include electron-phonon scattering in the NEGF simulator, considering both acoustic and optical phonons. The power factor of this geometry as the NI barrier height increases is shown in Fig. 3. The superlattice barrier height is indicated by the dashed line, The Fermi level is placed at E_F = 0.07 eV. Again, as above, for very low NI barrier heights, below the superlattice barrier and E_F, the influence of the NIs on the power factor is small, especially for lower densities. Higher densities reduce the power factor at high barrier heights, however the overall reduction is of the order of ~20%, which indicates that it might be worth to use high densities if the thermal conductivity is degraded by a larger amount. We are currently undertaking efforts to estimate the influence of NIs, voids and boundaries of various densities and configurations on the thermal conductivity. Although in this work we did not consider any specific material, we are also undertaking efforts using atomistic methods to include material specific parameters in the simulations.

III. Conclusions

In conclusion, we present a study of the thermoelectric power factor in nanostructured materials with nanoinclusions and superlattice-like barriers, geometries that are often employed to reduce the thermal conductivity of materials. We show that small barrier heights under degenerate conditions can have a very small positive effect on the power factor independent of nanoinclusion density, which could be a useful direction for obtaining large thermoelectric performance using nanostructures.

Acknowledgment

This work has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 Research and Innovation Programme (Grant Agreement No. 678763).

References

[1] K. Biswas, J. He, I. D. Blum, C.-I. Wu, T. P. Hogan, D. N. Seidman, V. P. Dravid and M. G. Kanatzidis, "High-performance bulk thermoelectrics with all-scale hierarchical architectures." Nature, 489, 414, 2012.

[2] 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 24, 205402, 2013.

[3] B. Lorenzi, D. Narducci, R. Tonini, S. Frabboni, G.C. Gazzadi, G. Ottaviani, N. Neophytou, X. Zianni, "Paradoxical enhancement of the power factor in polycrystalline silicon due to the formation of nanovoids," Journal of Electronic Materials, 43, 10, pp 3812-3816, 2014.

[4] N. S. Bennett, D. Byrne, A. Cowley, and N. Neophytou, "Dislocation Loops as a Mechanism for Thermoelectric Power Factor Enhancement in Silicon Nano-Layers," Appl. Phys. Lett. 109, 173905, 2016.

[5] M. Thesberg, H. Kosina, and N. Neophytou,'On the effectiveness of the thermoelectric energy filtering mechanism in low-dimensional superlattices and nano-composites', J. Appl. Phys. 120, 234302, 2016.

[6] R. Kim and M. S. Lundstrom, 'Computational study of energy filtering effects in one-dimensional composite nano-structures,' J. Appl. Phys., 111, 024508, 2012.

[7] T. Zou, X. Qin, Y. Zhang, X. Li, Z. Zeng, D. Li, J. Zhang, H. Xin, W. Xie, A. Weidenkaff, "Enhanced thermoelectric performance of β-Zn_4Sb_3 based nanocomposites through combined effects of density of states resonance and carrier energy filtering" *Scientific Reports*, 5, 17803, 2015.

[8] S. Foster, M. Thesberg, N. Neophytou, "Thermoelectric power factor of nanocomposite materials from two-dimensional quantum transport simulations", *Physical Review B*, 96, 195425, 2017.

[9] V. Vargiamidis, S. Foster, N. Neophytou, "Thermoelectric power factor in nanostructured materials with randomized nanoinclusions", *Physica Status Solidi A*, (accepted).