TAILORING ELECTRON AND PHONON ENERGY DISPERSION AND THERMAL TRANSPORT IN NANO- AND MICROARCHITECTURES

V. M. Fomin[1,2]

[1]*Institute for Integrative Nanosciences, Leibniz Institute for Solid State and Material Research, Dresden, Dresden, D-01069 Germany*
[2]*Department of Theoretical Physics, Department of Physics and Engineering, Moldova State University, Chisinau, MD-2009 Republic of Moldova*
E-mail: v.fomin@ifw-dresden.de

(Received August 8, 2018)

1. Introduction

The use of nontrivial geometry and topology for effective tailoring physical properties of diversified quantum fields in novel micro- and nanostructures is one of the most appealing avenues in modern nanophysics and nanotechnologies [1]. Analysis of topologically nontrivial manifolds at the nanoscale is of immense importance for semiconductor, superconductor, and graphene physics as well as for optics, magnetism, and quantum computing. The highly diversified investigations underpin development of promising low-cost high-performance electronic, spintronic, optoelectronic, optical memory, and information processing technology based on quantum rings and related nanoarchitectures. Nanostructuring,as suggested more than two decades ago [2], creates a timely opportunity to search for new advanced thermoelectric materials (see [3, 4] for reviews).

Thermoelectric energy conversion efficiency is quantified by the figure of merit

$$ZT = \frac{S^2 \sigma T}{\kappa_{ph} + \kappa_{el}},$$

where$S$ is the Seebeck coefficient, σ is the electrical conductivity, $T$is the absolute temperature,κ_{ph} and κ_{el} are the phononand electron thermal conductivities, respectively. The electron thermal conductivity is usually much smaller than the phonon one. The phonon thermal conductivity is usually dominated by acoustic phonons because of their higher group velocity and lower energy (resulting in higher population factors) as compared with optical phonons. The ambitious task for advancing thermoelectric applications is thus to create materials that would combine properties of (i) electronic metals with high values of the Seebeck coefficient and electric conductivity and (ii) phonon insulators with low values of the phonon thermal conductivity. In what follows, some of the results in the field are overviewed from the point of view of the present author's scientific interests.

The development of subbands of electron spatial quantization in 1D stacks of quantum dots (or, equivalently, segmented nanowires (NWs)) allows for an efficient control over the Seebeck coefficient and the electrical conductivity [5], phonon-engineered thermal transport in NWs with constant and periodically modulated crosssections as well as with core–shell structure [6–8]. A decrease in phonon group velocities in combination with an enhancementof phonon

boundary scattering implies a significant reduction of the phonon lattice thermal conductivitycompared with bulk.

Efficient engineering acoustic phonon energy spectrum has been searched for in rolled-up multishell tubular structures. The strain-driven roll-up procedure is an available instrument for the preparation of multilayer micro- and nanosuperlattices (SLs) and their arrays [9–11]. The acoustic phonon dispersion in multishell tubular structures has been analyzed in terms of elastodynamics [12]. It has been shown that the number of shells is an important controlparameter of the phonon dispersion together with the structure dimensions and acousticimpedance mismatch between the shells.Anincrease in the number of shells has been demonstrated to lead to an appreciable decrease in the average and rms phonon groupvelocities.

2. Effect of the Miniband Energy Spectrum on the Electronic Transport Characteristics in a Periodic 1D Stack of Disk-Shaped InAs/GaAs Quantum Dots (QDs)

An approach for numerical calculationof the electron dispersion, the transport relaxation time, and the transport coefficients in a periodic 1D stack of disk-shapedInAs/GaAs QDs (1D QD SL)has been developed [5].We study the effect of narrow electronic minibands(Fig. 1) in periodic 1Dstacks of disk-shapedInAs QDsin GaAs on their electronic transport characteristics by employing anempirical tight-binding calculation and a continuum model of the electronic structure. Our model includes boththe minibands and the continuum of the host conduction band. By calculating the relaxation time foracoustic-phonon scattering explicitly, we show that the popularapproximation of a constant relaxation time is not adequatefor cross-plane transport through a stack of semiconductorQDs.

From the numerical analysis of the electric andthermal conductivities, the Seebeck coefficient and thefigure-of-merit, we conclude that electronic signatures ofnanostructuringshould be detectable in the thermoelectricresponse of a 1D stack of QDs. For judiciously chosen valuesof the donor concentration, depending on the geometricalparameters of the QD SL (see Fig. 2), the thermoelectric powerfactor is strongly enhanced. Hence, a QD SL exemplifiesa material, whose efficiency as a thermoelectricconverter is controlled bygeometry on the nanoscale.The thermoelectric figure-of-merit as a function of the donorconcentration represents the miniband electron energy spectrumof the QD stackand thus can be used as an experimentalfingerprint of the electronic structure of it. This method works best for low temperatures and flat QDs.

The highestZT values are achieved for QDs separated by extremely thinspacer layers, when the miniband features in transport mergewith the background due to the conduction band of the hostmaterial. For the system studied, InAs QDs inGaAs, the predicted figure-of-merit achieves, at an optimum nabnoarchitecture of the stack, maximal values of about 2.7, assuming the achieved phonon heat conductivity values of κ_{ph}~0.5 W $m^{-1}K^{-1}$(see the forthcoming Sections). Our results imply thatfor technical operation of QD SLs as thermoelectricconverters,the choice of the *optimum nanoarchitecture* and *doping concentration* is of paramount importance.

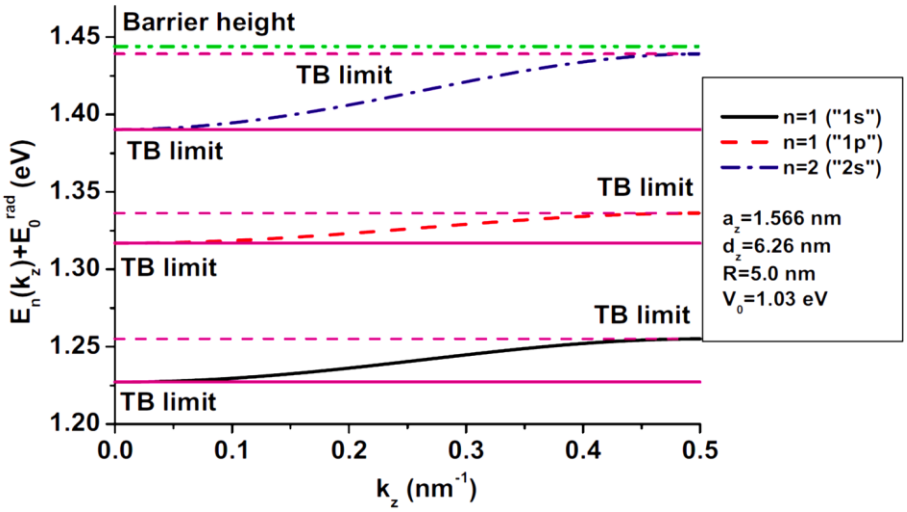


Fig. 1. Renormalized minibands in a 1D stack of InAs/GaAs QDs with geometrical parameters indicated in the inset. The valence band top of GaAs is taken as the zero of the energy. The dash-dotted line represents the position of the barrier (reprinted from [5]).

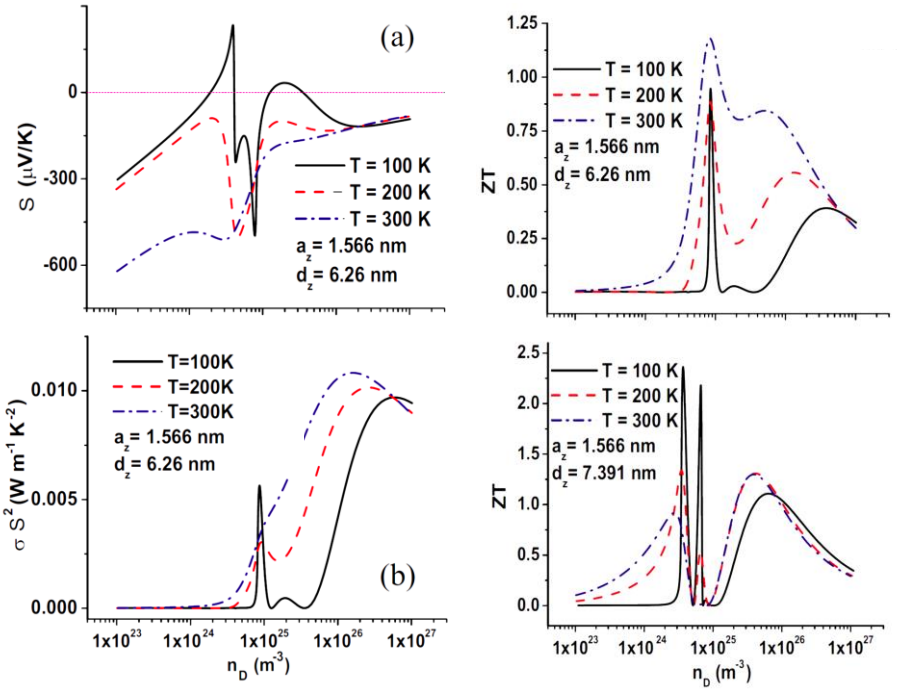


Fig. 2. Left panel: (a) the Seebeck coefficient and (b) the power factor in a stack of InAs/GaAs QDs. Right panel: the figure-of-merit for stacks of InAs/GaAs QDs with geometric parameters indicated in the insets (after [5]).

3. Phonon Filtering and Reduction of Lattice Thermal Conductivity in One-Dimensional QD SLs

It hasbeen theoretically shown that one-dimensional QD SLs (1D-QDSLs) consisting of acoustically mismatched materials exhibit sub-1 W $m^{-1}K^{-1}$ thermal conductivity in atemperature range of 50–400 K. Coherent Si/Ge 1D-QDSLs, as well as model Si/plastic, Si/SiO_2, and Si/SiC 1D-QDSLs, have been studied [6].The phonon energy spectra and group velocities areobtained in

terms of the Face-Centered Cubic-Cell model of the Born–von Karman (BvK)-approach to lattice dynamics. On this basis, lattice thermal conductivity is calculated within the Boltzmann transport equation. A strong reduction of latticethermal conductivity in 1D-QDSL structures in comparison with homogeneous rectangular Si NWs (Fig. 3) is attributed to the exclusion of phonon modes folded in SL segments from the heat flow and thedecelerating action of Ge, SiO_2, or plastic materials. Thus, the 1D-QDSL structures act as effective *phonon filters* and thereby eliminate a significant number of phonon modes from thermal transport. The obtained results imply that QDSLs are promising as thermoelectric materials and thermal insulators.

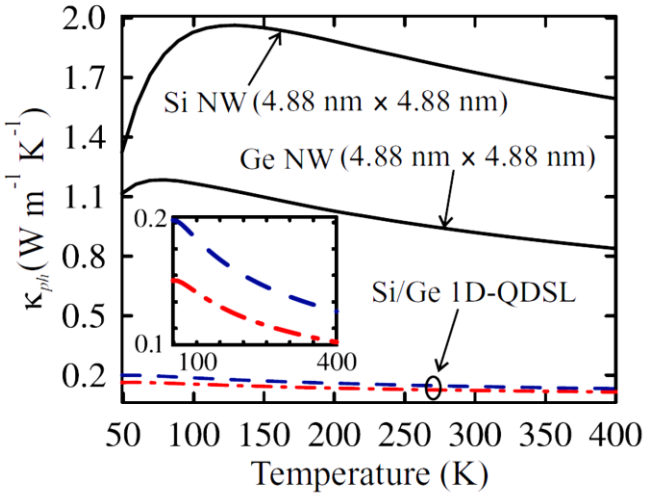


Fig. 3. Temperature dependence of lattice thermal conductivity for Si and Ge homogeneous NWs (solid lines) and for Si/Ge 1D-QDSLs with six atomic layers of Si and two atomic layers of Ge (dashed line) and with four atomic layers of Si and four atomic layers of Ge (dash-dotted line) per SL period. The inset shows a magnified view of the above temperature dependence of thermal conductivity for 1D-QDSLs (reprinted from [6]).

4. Suppression of Phonon Heat Conduction in Cross-Section-Modulated NWs (MNWs)

We have theoretically shown that a phonon heat flux can be significantly suppressed in Si and Si/SiO_2NWs with a periodically modulated cross-section area, which is referred to as the *cross-section-MNWs*, compared with the generic uniform cross-section NWs. The phonon energy spectra were obtained using the five-parameter BvK approach and the Face-Centered-Cubic-Cellmodel for description of the lattice dynamics. The thermal flux and thermal conductivity in Si and Si/SiO_2cross-section-MNWs are calculated using the Boltzmann transport equation within the relaxationtime approximation. Redistribution of the phonon energy spectra in the cross-section-MNWsleads to a strong decrease in the average phonon group velocities and a respective suppression of thephonon thermal flux in these NWs compared with the generic NWs. This effect is attributed to the exclusion of the phonon modes trapped in the segments of cross-section-MNWs from the heat flow. As a result, a three- to sevenfold drop in the phonon heat flux in atemperature range of 50–400K is predictedfor Si and Si/SiO_2 cross-section-MNWs under consideration. The obtained results indicate thatcross-section-MNWs are promising candidates for thermoelectric applications.

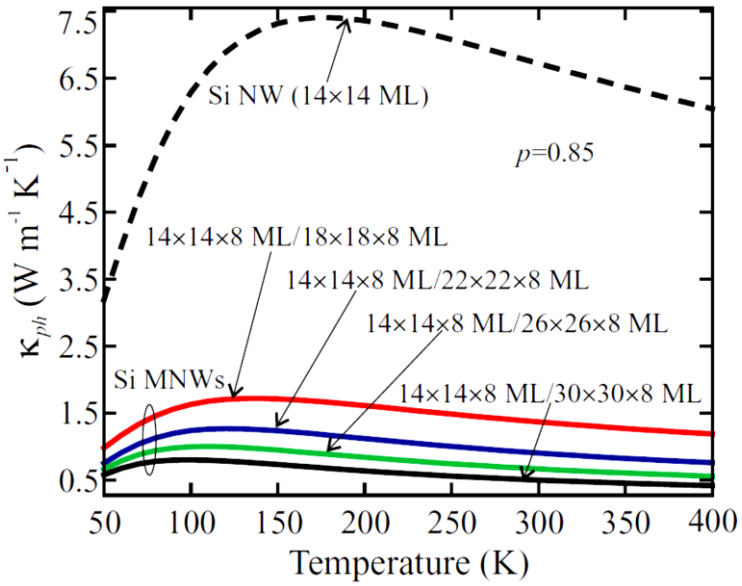


Fig. 4. Temperature dependence of the lattice thermal conductivity in the Si NW with the cross section of 14 × 14 ML and the various Si cross-section-MNWs with geometric parameters given in the insets (reprinted from [7]).

Our results show that, for all values of specularity parameter *p*under consideration, the thermal flux carried by the long-wavelength phonon modesin MNWs islowerby a factorof ~5than that inNWs due to *phonon trapping*.An increase in *p*leads to a decrease in the thermal flux carried by the long-wavelength phonon modes and strongly enhances the thermal flux carried by the rest of the phonon modesin NWs due to attenuation of the boundary scattering of thehigh-energy phonon modes. These modes in MNWsare not involved in the heat transfer because of their localization inthe wide segments. For this reason, the ratio between thermalfluxes in the NW and MNWs appreciably depends on specularity parameter *p* (Fig. 5).

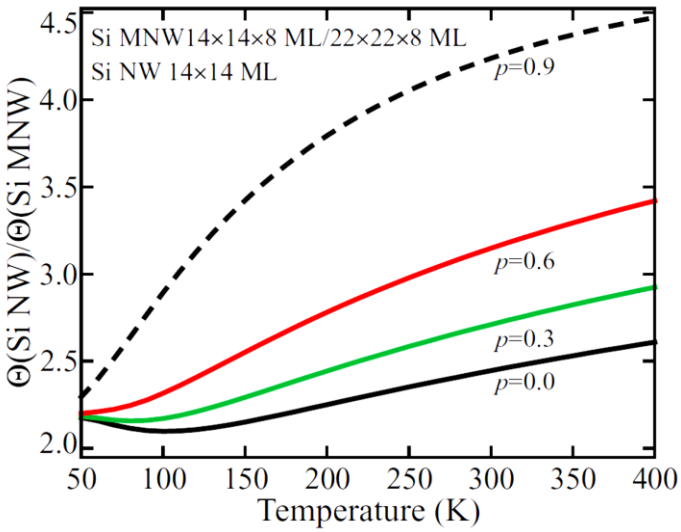


Fig. 5. Temperature dependence of the ratio of thermal fluxes in the Si NW and the Si MNW. The results are shown for different values of specularity parameter *p* = 0.0, 0.3, 0.6, and 0.9 (reprinted from [7]).

5. Phonon-Engineered Thermal Transport in Si Wires: A Crossover between Nano- and Microscale Regimes

More recently, we have theoretically studied the transition between nanoscale and microscale thermal transport regime at room temperature in Si wires with constant and periodically modulated cross-section. Extrapolating the calculated thermal conductivity from the nano- to micrometer range, we find thecharacteristic dimensions of the wires, where a crossover between nanoscale and microscale thermaltransport occurs. This crossover is observed in both generic (smooth) and cross-section-modulated wires. In case of smooth Si wires, we reveal a strong dependence of the crossing point positionon the boundary roughness. For silicon wires with weak boundary roughness, the crossover (Fig. 6) occursat crosssections of 60 × 300 nm, while for very rough boundaries it occurs at crosssections of 150 × 750 nm. In case of periodically modulated wires, the crossover between nano- andmicroscale regimes occurs at typical crosssections of 120 × 120 nm of the narrow segment, andit is almost independent of boundary roughness. A strong distinction from the case of smooth wiresis attributed to (i) different trends of the phonon thermal conductivity at the nanometer scale, wherefrom the extrapolation was performed,and (ii) different phonon–boundary scattering due to the specific geometry. Formodulated silicon wires, the effect of the modulation thickness, the modulation length, and the cross-sectionalarea on the phonon thermal conductivity at the room temperature is analyzed. A possibilityof thermal transport engineering in cross-section-modulated wires by resizing them is revealedin both nano- and microscale regimes. The presented results pave the way towards a better understandingof thermal transport reduction in Si NWs with engineered diameter modulations andshed light on the *crossover between nano- and microscale regimes* of thermal transport.

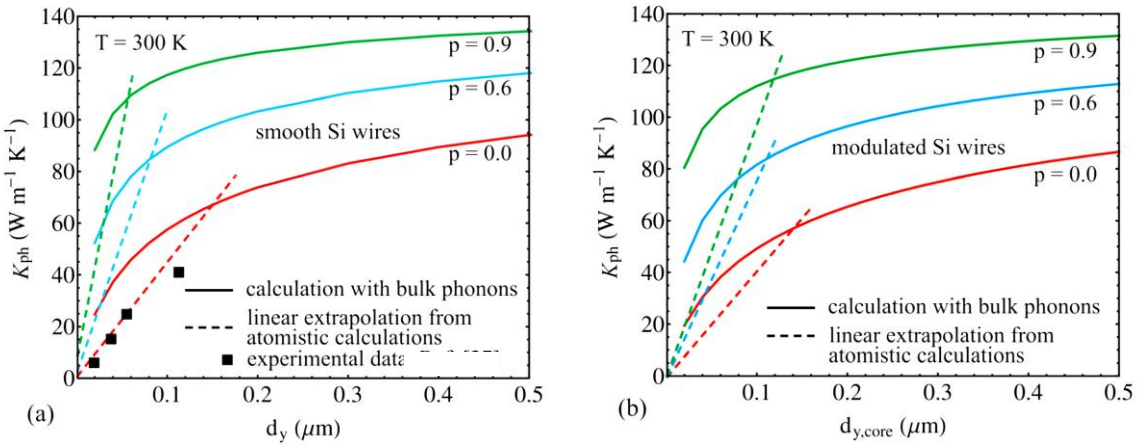


Fig. 6. Room-temperature phonon thermal conductivity: (a) as a function of the cross-section size of smooth Si wires and (b) as a function of core thickness d_y of square-cross-section modulated Si wires for different values of specularity parameter p = 0, 0.6, and 0.9. Filled squares denote experimental data from [13] (reprinted from [8]).

6. In-Plane Thermal Conductivity of Radial and Planar Si/SiO_xHybridNanomembraneSLs

Althoughsilicon has been widely used in modern electronic devices, it has not yetbeenimplemented in thermoelectric applications mainly due tohigh thermal conductivity

κ,which leads to an extremely low figure ofmerit. An approach to manage κ of Si thin-film based nanoarchitectures has been designed through the formation of radial and planar Si/SiO_x hybrid nanomembraneSLs(HNMSLs). For radial Si/SiO_x HNMSLs with different numbers of windings (1, 2, and 5), which are produced by a high-tech method of strain-driven self-assembly (roll-up), a continuous reduction in κ with an increase in the number of windingsis observed (Fig. 7).Meanwhile, the planar Si/SiO_x HNMSL, which is prepared by mechanically compressing a five-windingrolled-up microtube, shows the smallest in-plane thermal conductivity among allthe reported values for Si-based SLs. A theoretical model is proposed within theframework of the BvKapproach to lattice dynamics to quantitatively interpret theexperimental data (Fig. 8). The average phonon group velocities are calculated overthe entire Brillouin zone. The results are plotted as a function of phonon energy in Fig. 8 (left panel). ForSi/SiO_2 HNMSL, average is taken for a particular component of the phonon group velocity (in-plane or cross-plane). The figure reveals an appreciable effect of the phonon confinement on phonon energy dispersion and group velocities in Si/SiO_2 HNMSLs. It is significant that there appear hybrid modes propagating in the whole structure, rather than separate vibrational modes in individual Si or SiO_2 layers. Figure 8 (right panel) shows theoretical results for the lattice thermal conductivity for HNMSL with amorphous SiO_2 layers at different values of mean vibrational energy$\langle E \rangle$: 34meV (purple curve), 53 meV (black curve), and 70 meV (green curve), alongwith those for HNMSL with crystalline α-quartz layers (gray curve). The performed analysis indicates that the thermal conductivity of Si/SiO_x HNMSLs is largely determined by the phonon processes in the SiO_x layers.

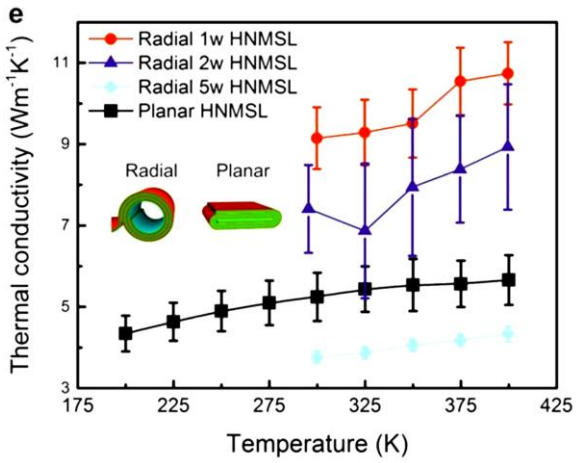


Fig. 7. Experimental in-plane thermal conductivities of planar (black squares) and radial (red circles for one-winding, purple triangles for two-winding and cyan diamonds for five-winding) Si/SiO_x HNMSLs as a function of temperature (reprinted from [11]).

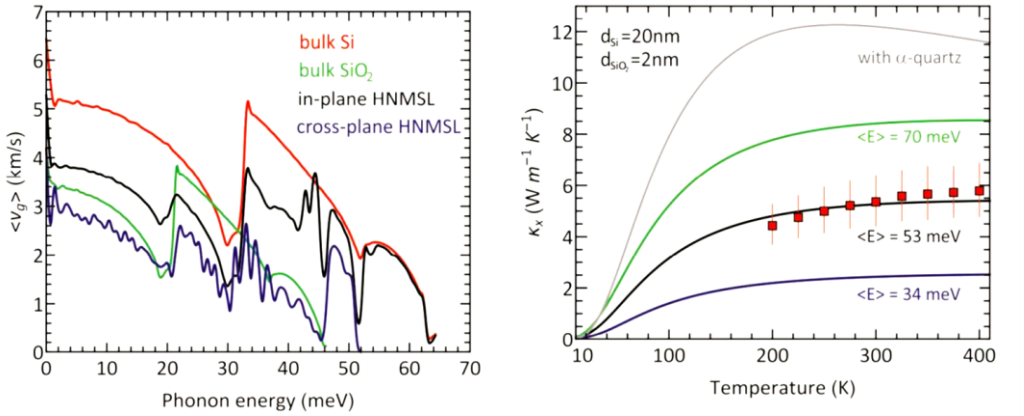


Fig. 8. Theoretical model for planar Si/SiO_2 HNMSLs: (a) schematic structure of a planar Si/SiO_2 HNMSL with a SL period consisting of 2-nm SiO_2, 20-nm Si, and 2-nm SiO_2. Left panel: average phonon group velocity as a function of phonon energy for the Si/SiO_2 HNMSL (black curve, in-plane component; purple curve, cross-plane component), bulk Si (red curve), and bulk SiO_2 (green curve). Right panel: in-plane lattice thermal conductivity as a function of temperature in the Si/SiO_2 HNMSL. Red solid squares denote the experimental data (reprinted from [11]).

7. Phonon Spectrum Engineering in Rolled-Up Micro- and Nanoarchitectures

The strain-driven roll-up procedurepaves the way for novel classes of metamaterials, such as single semiconductor radialmicro- and nanocrystals and multilayer radial micro- and nanosuperlattices. We have analyzed a possibility of efficient engineering of the acoustic phonon energy spectrum in multishell tubular structures, which provide a model for radial SLs [12]. The acousticphonon dispersion is determined by solving the equations of elastodynamics for constituent (InAs/GaAs or Si/SiO_2) bi-material systems. It is shown that the total number of shells N_L is an important controlparameter of the phonon dispersion alongwith the structure dimensions and acousticimpedance mismatch between the SL layers. The obtained results suggest thatrolled-up nanoarchitectures are promising for thermoelectric applications owing to apossibility of significant reduction of the thermal conductivity without degradation of theelectronic transport

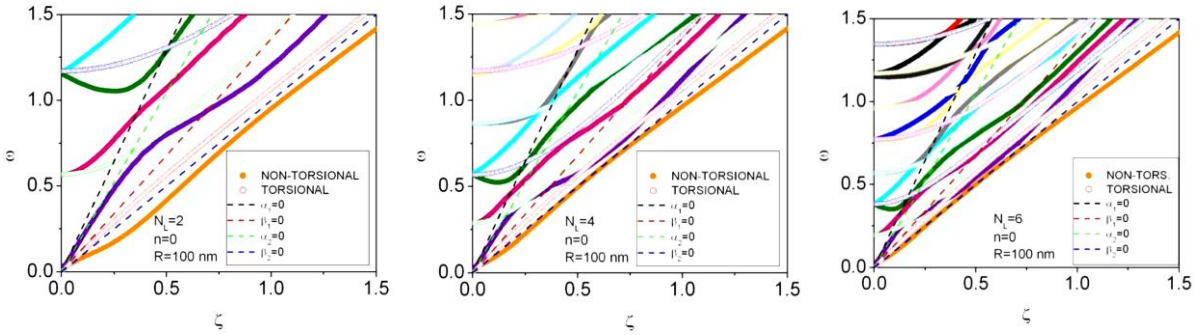


Fig. 9. Phonon dispersion curves for $n = 0$ and $N_L = 2, 4, 6$. The inner and outer radii of the InAs/GaAs multishelltubesare $r_0 = 100$ nm and $r_2 = 110$ nm, $r_4 = 120$ nm, $r_6 = 130$nm, respectively. Non-torsional and torsional modes are represented by filled and empty circles, respectively. The dashed lines indicate the dispersion curves for dilatational ($\alpha_i = 0$) and shear ($\beta_i = 0$) waves (reprinted from [12]).

To visualize the overall impact of the number of layers in a multishelltube on thegroup velocity, the average and rms phonon group velocities are calculated for the branchesavailable from the above results (see Fig. 10).At small wave vectors, the average and rmsphonon group velocitiesdecrease with increasing N_L.

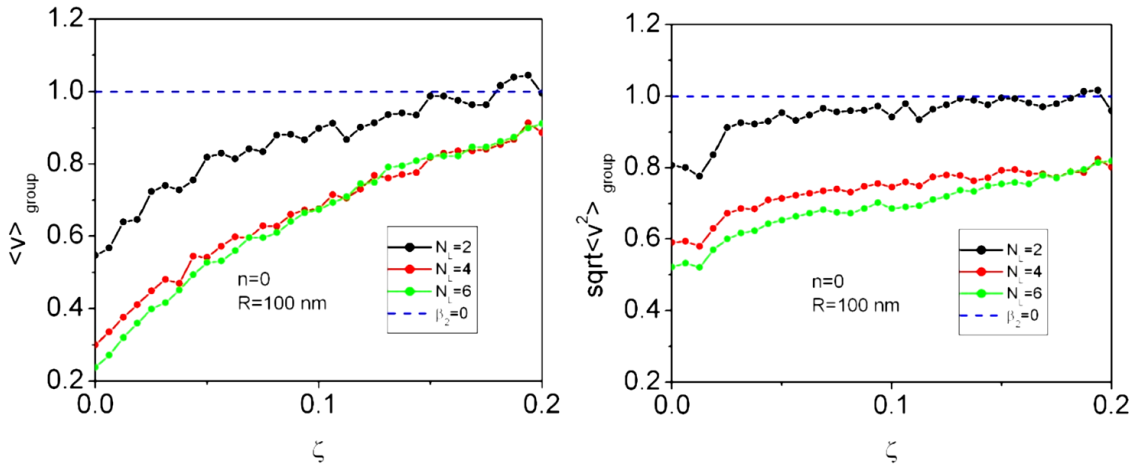


Fig. 10. Average (left panel) and rms phonon group velocity dispersion curves (right panel) for $n = 0$ at $N_L = 2$, 4, and 6 (reprinted from [12]).

Phonon dispersion curves in Si/SiO_2multishelltubeswith two and four shells are shown in Fig. 11, wherethe dimensional unit is ~5 meVforphonon energy $\hbar\omega$and ~5×10^8 $m^{-1}$for thewave number. With increasing wave number, more phonon modes reveal an appreciable dispersion and therefore provide a larger contribution to the thermal conductivity. The dispersion curves of non-torsional modes in a multishell structure exhibit significant kinks when hitting the dispersion curve of a Rayleigh wave at the surface of Si corresponding to the dispersion relation of a dilatational waveα_1=0. The dispersion curves of torsional modes in a multishell structure exhibit moderate kinks when hitting the dispersion curve of a Rayleigh wave at the surface of SiO_2 stemming from the dispersion relation of a shear wave β_2=0.

The calculated phonon density of states (DOS) reveals almost equidistant peaks typical of a 1D quantum wire(Fig. 12). This fact sheds light on the nature of the vibrational excitations in multishell tubes. The corresponding average group velocity (green) as a function of energy represents the spectral structure of the phonon DOS. The periods of DOS exhibit a hyperbolic dependence on the number of shells NL with high accuracy. Similarly to Fig. 10, phonon group velocity calculated for long-wave phonons in Si/SiO_2multishelltubes systematically decreases within increasing N_L.

In the framework of the ongoing research [14], an atomistic calculation is applied to tackle the phonons and thermal transport in multishell nanotubes.

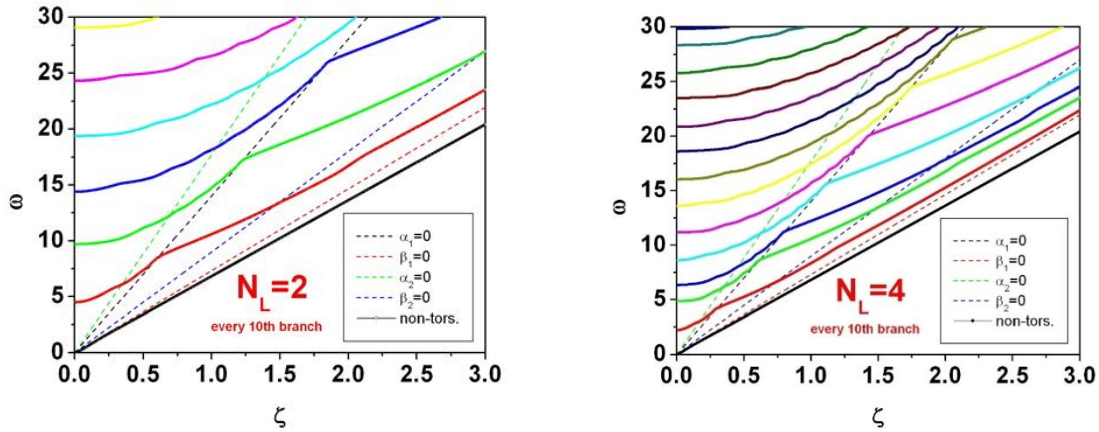


Fig. 11. Phonon dispersion curves for Si/SiO_2 multishell nanotubes with $N_L = 2$ and 4. The inner radius is r_0=1050 nm; the thicknesses of the Si and SiO_2 shells are 18 and 2 nm, respectively.

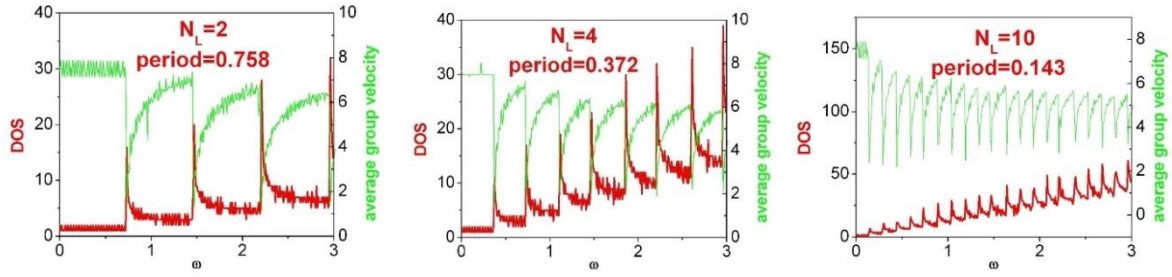


Fig. 12. Phonon DOS and average group velocity for Si/SiO_2 multishell nanotubes with $N_L = 2$, 4, and 10. The inner radius is r_0=1050 nm; the thicknesses of the Si and SiO_2 shells are 18 and 2 nm, respectively.

Conclusions

For various micro- and nanoarchitectures, we have found a possibility of efficiently engineeringthe Seebeck coefficient and electric conductivity in 1D stacks of QDs, acousticphonon energy dispersion in 1DQD SLs, cross-section-MNWs, Si wires ranging from nanoscale to microscale, and, more recently, multishell tubular structures.The changes in the acoustic phonon spectrum and their effect on phonon transport have been experimentally detected in first thermal conductivity measurements. Further studies are required to show that a reduction in the phonon group velocity and phonon thermal conductivity can be achieved without significant roughness scattering and degradation of electron transport.Our resultssuggest that 1D stacks of QDs (1D QD SLs), cross-section-modulated micro- and nanowires, as well as arrays of rolled-up radial SLs, are promising candidates foran advancement in thermoelectric materials and devices.

Acknowledgments.I gratefully acknowledge collaborations with A.A. Balandin, C.I. Isacova, A.I. Cocemasov, D.L. Nika, D. Grimm, G. Li, K. Manga,A. Mavrokefalos, F. Zhu, and O.G. Schmidt. This work has been supported by the German Research Foundation (DFG) through grant no. FO-956/4-1 MULTISHELL.

References

[1] V.M. Fomin, Topology-driven effects in advanced nanoarchitectures, in: A. Sidorenko (Ed.), Functional Nanostructures and Metamaterials for Superconducting Spintronics, Springer International Publishing, Cham, 2018, pp. 195–220.
[2] L. Hicks and M. Dresselhaus,Phys. Rev. B47, 12727 (1993).
[3] M.S. Dresselhaus, G. Chen, M. Y. Tang, R. G. Yang, H. Lee, D. Z. Wang, Z. F. Ren, J.-P. Fleurial, and P. Gogna,Adv. Mater. 19, 1043 (2007).
[4] A.A. Balandin and D.L. Nika, Mater. Today 15 (6), 266 (2012).
[5] V. M. Fomin and P. Kratzer, Phys. Rev. B 82, 045318 (2010).
[6] D.L. Nika, E.P. Pokatilov, A.A. Balandin, V.M. Fomin, A. Rastelli, and O.G. Schmidt, Phys. Rev. B 84, 165415 (2011).
[7] D.L. Nika, A.I. Cocemasov, C.I. Isacova, A.A. Balandin, V.M. Fomin, and O.G. Schmidt, Phys. Rev. B 85, 205439 (2012).
[8] A.I. Cocemasov, D.L. Nika, V.M. Fomin, D. Grimm, and O.G. Schmidt, Appl. Phys. Lett. 107, 011904 (2015).
[9] D. Grimm, R.B. Wilson, B. Teshome, S. Gorantla, M.H. Rümmeli, T. Bublat, E. Zallo, G. Li, D.G. Cahill, and O.G. Schmidt, Nano Lett. 14, 2387 (2014).
[10] G. Li, D. Grimm, V. Engemaier, S. Lösch, K. Manga, V. K. Bandari, F. Zhu, and O.G. Schmidt, Phys. Status Solidi (A) 213, 620 (2016).
[11] G. Li, M. Yarali, A. Cocemasov, S. Baunack, D. L. Nika, V. M. Fomin, S. Singh, T. Gemming, F. Zhu, A. Mavrokefalos, and O.G. Schmidt, ACS Nano 11, 8215 (2017).
[12] V.M. Fomin and A.A. Balandin, Appl. Sci. 5, 728 (2015).
[13] D. Li, Y. Wu, P. Kim, L. Shi, P. Yang, and A. Majumdar, Appl. Phys. Lett. 83, 2934 (2003).
[14] C. I. Isacova,A. I. Cocemasov, D. L. Nika, and V.M. Fomin (under preparation).