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

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(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, $\sigma$ is the electrical conductivity, $T$ is the absolute
temperature, $\kappa_{ph}$ and $\kappa_{el}$ are the phonon and 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 enhancement of phonon
boundary scattering implies a significant reduction of the phonon lattice thermal conductivity compared 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 control parameter of the phonon dispersion together with the structure dimensions and acoustic impedance mismatch between the shells. An increase in the number of shells has been demonstrated to lead to an appreciable decrease in the average and rms phonon group velocities.

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 calculation of the electron dispersion, the transport relaxation time, and the transport coefficients in a periodic 1D stack of disk-shaped InAs/GaAs QDs (1D QD SL) has been developed [5]. We study the effect of narrow electronic minibands (Fig. 1) in periodic 1D stacks of disk-shaped InAs QDs in GaAs on their electronic transport characteristics by employing an empirical tight-binding calculation and a continuum model of the electronic structure. Our model includes both the minibands and the continuum of the host conduction band. By calculating the relaxation time for acoustic-phonon scattering explicitly, we show that the popular approximation of a constant relaxation time is not adequate for cross-plane transport through a stack of semiconductor QDs.

From the numerical analysis of the electric and thermal conductivities, the Seebeck coefficient and the figure-of-merit, we conclude that electronic signatures of nanostructures should be detectable in the thermoelectric response of a 1D stack of QDs. For judiciously chosen values of the donor concentration, depending on the geometrical parameters of the QD SL (see Fig. 2), the thermoelectric power factor is strongly enhanced. Hence, a QD SL exemplifies a material, whose efficiency as a thermoelectric converter is controlled by geometry on the nanoscale. The thermoelectric figure-of-merit as a function of the donor concentration represents the miniband electron energy spectrum of the QD stack and thus can be used as an experimental fingerprint of the electronic structure of it. This method works best for low temperatures and flat QDs.

The highest ZT values are achieved for QDs separated by extremely thin spacer layers, when the miniband features in transport merge with the background due to the conduction band of the host material. For the system studied, InAs QDs in GaAs, the predicted figure-of-merit achieves, at an optimum nanobonoarchitecture of the stack, maximal values of about 2.7, assuming the achieved phonon heat conductivity values of $\kappa_{ph} \approx 0.5 \text{ W m}^{-1}\text{K}^{-1}$ (see the forthcoming Sections). Our results imply that for technical operation of QD SLs as thermoelectric converters, 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 has been theoretically shown that one-dimensional QD SLs (1D-QDSLs) consisting of acoustically mismatched materials exhibit sub-1 W m\(^{-1}\)K\(^{-1}\) thermal conductivity at temperature 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 are obtained 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 lattice thermal 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 the decelerating action of Ge, SiO₂, 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/SiO₂ NWs 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-Cell model for description of the lattice dynamics. The thermal flux and thermal conductivity in Si and Si/SiO₂ cross-section-MNWs are calculated using the Boltzmann transport equation within the relaxation time approximation. Redistribution of the phonon energy spectra in the cross-section-MNWs leads to a strong decrease in the average phonon group velocities and a respective suppression of the phonon 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 a temperature range of 50–400 K is predicted for Si and Si/SiO₂ cross-section-MNWs under consideration. The obtained results indicate that cross-section-MNWs are promising candidates for thermoelectric applications.
Our results show that, for all values of specularity parameter $p$ under consideration, the thermal flux carried by the long-wavelength phonon modes in MNWs is lower by a factor of ~5 than that in NWs 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 modes in NWs due to attenuation of the boundary scattering of the high-energy phonon modes. These modes in MNWs are not involved in the heat transfer because of their localization in the wide segments. For this reason, the ratio between thermal fluxes in the NW and MNWs appreciably depends on specularity parameter $p$ (Fig. 5).
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 the characteristic dimensions of the wires, where a crossover between nanoscale and microscale thermal transport 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 position on the boundary roughness. For silicon wires with weak boundary roughness, the crossover (Fig. 6) occurs at 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- and microscale regimes occurs at typical crosssections of 120 × 120 nm of the narrow segment, and it is almost independent of boundary roughness. A strong distinction from the case of smooth wires is 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. For modulated silicon wires, the effect of the modulation thickness, the modulation length, and the cross-sectional area on the phonon thermal conductivity at the room temperature is analyzed. A possibility of thermal transport engineering in cross-section-modulated wires by resizing them is revealed in both nano- and microscale regimes. The presented results pave the way towards a better understanding of thermal transport reduction in Si NWs with engineered diameter modulations and shed 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]).](image)

6. In-Plane Thermal Conductivity of Radial and Planar Si/SiO$_2$ Hybrid Nanomembrane SLs

Although silicon has been widely used in modern electronic devices, it has not yet been implemented in thermoelectric applications mainly due to high thermal conductivity
\( \kappa \), which leads to an extremely low figure of merit. An approach to manage \( \kappa \) of Si thin-film based nanoarchitectures has been designed through the formation of radial and planar Si/SiO\(_x\) hybrid nanomembrane SLs (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 \( \kappa \) with an increase in the number of windings is observed (Fig. 7). Meanwhile, the planar Si/SiO\(_x\) HNMSL, which is prepared by mechanically compressing a five-winding rolled-up microtube, shows the smallest in-plane thermal conductivity among all the reported values for Si-based SLs. A theoretical model is proposed within the framework of the BvK approach to lattice dynamics to quantitatively interpret the experimental data (Fig. 8). The average phonon group velocities are calculated over the entire Brillouin zone. The results are plotted as a function of phonon energy in Fig. 8 (left panel). For Si/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 \( \langle E \rangle \): 34 meV (purple curve), 53 meV (black curve), and 70 meV (green curve), along with those for HNMSL with crystalline \( \alpha \)-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 multishell tube on the group velocity, the average and rms phonon group velocities are calculated for the branches available from the above results (see Fig. 10). At small wave vectors, the average and rms phonon group velocities decrease 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]).](image)

Phonon dispersion curves in Si/SiO\(_2\) multishell tubes with two and four shells are shown in Fig. 11, where the dimensional unit is \( \sim 5 \) meV for phonon energy and \( \sim 5 \times 10^{8} \) m\(^{-1}\) for the wave 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 wave \( \alpha_1 = 0 \). 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 \( \beta_2 = 0 \).

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 \( N_L \) with high accuracy. Similarly to Fig. 10, phonon group velocity calculated for long-wave phonons in Si/SiO\(_2\) multishell tubes 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 engineering the Seebeck coefficient and electric conductivity in 1D stacks of QDs, acoustic phonon 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 results suggest 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 for 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.
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