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Topical Review

Phononic pathways towards rational design of nanowire heat conduction

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Abstract

Thermal conduction in semiconductor nanowires is controlled by the transport of atomic vibrations also known as thermal phonons. The ability of nanowires to tailor the transport of thermal phonons stems from their precise atomic scale growth coupled with high structural surface to volume ratios. Understanding and manipulating thermal transport properties at the nanoscale is central for progress in the fields of microelectronics, optoelectronics, and thermoelectrics. Here, we review state-of-the-art advances in the understanding of nanowire thermal phonon transport and the design and fabrication of nanowires with tailored thermal conduction properties. We first introduce the basic physical mechanisms of thermal conduction at the nanoscale and detail recent developments in employing nanowires as thermal materials. We discuss and provide insight on different strategies to modulate nanowire thermal properties leveraging the underlying phonon transport processes occurring in nanowires. We also highlight challenges and key areas of interest to motivate future research and create exceptional capabilities to control heat flow in nanowires.

Keywords: nanowires, phonon transport, heat conduction

(Some figures may appear in colour only in the online journal)

1. Introduction

Generating heat and controlling its transport has been an integral component of technological progress over millennia. From the discovery of fire to the industrial revolution via the steam engine, the path of human progress has been paved by the improved ability to direct thermal energy. Control of thermal energy flow is now central to the performance of electronic and optoelectronic devices, efficiency of energy materials such as thermoelectrics, industrial processes, and energy control in homes and buildings. For example, a modern-day nanometer scale electronic processor can generate local thermal fluxes rivaling those received by the Earth from the Sun, which need to be effectively dissipated for efficient performance of laptops, tablets, and supercomputers [1–3]. In addition, thermoelectric devices which convert heat into electricity require semiconductor materials with low thermal conductivities in order to enhance their efficiency [4, 5]. Due to its ubiquity, thermal energy transport thus remains central to current technological development. Building upon the seminal work by Fourier on bulk continuous materials [6], we have reached a point where the thermal behavior of systems can be understood and controlled from the perspective of atoms arranged in a crystal lattice [7]. From this atomic perspective, thermal transport in nonmetallic crystalline solids is described as the transport of atomic vibrations with broadband frequencies that are generated and move under an applied temperature gradient. Understanding and manipulating the movement of these lattice thermal vibrations is critical to gain full control of heat conduction in crystalline solid materials. In recent years, progress in experimental methods in nanotechnology has

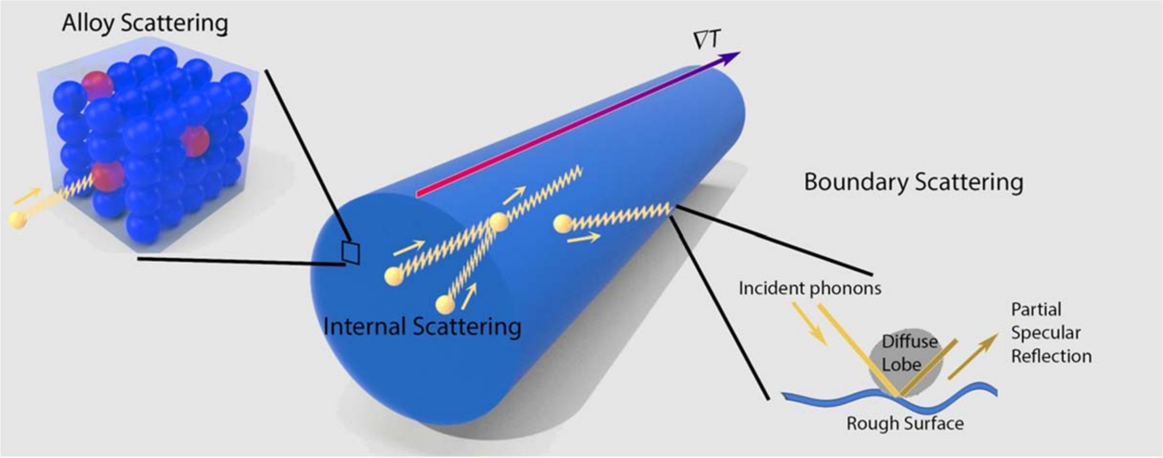

Figure 1. Schematic of phonon scattering mechanisms in semiconductor nanowires. Within the nanowire, phonons (yellow) can interact with each other (phonon–phonon scattering) as well as with point defects (inset, red atoms) in the crystal lattice (phonon-defect scattering). In addition to internal scattering, phonons can also interact with the nanowire boundary where a portion of them are scattered diffusively by the rough interface (phonon-boundary scattering). All these scattering processes hinder the flow of heat along the applied temperature gradient.

allowed for precise fabrication of small-scale structures with unique thermal properties not seen at the bulk macroscopic scale. Manipulating the transport of atomic vibrations at small length scales lies at the heart of controlling thermal conduction via nanostructured materials. In particular, the rational design of nanostructures, both in its top-down and bottom-up paradigm, provides a unique ability to create engineered materials with tailored thermal properties suited for scientific and technological applications.

In this review, we discuss recent developments and provide insights on manipulating thermal transport in one-dimensional semiconductor nanostructures. In recent years, these nanostructures have exhibited significant potential in the design and fabrication of materials for targeted applications including advanced thermoelectrics [8, 9], electronics [10, 11], optoelectronics [12, 13] and catalysis [14, 15]. One-dimensional nanostructures are of special interest because of their high surface-to-volume ratios which can strongly modify the thermal transport properties of materials. The continuing advances in both top-down and bottom-up growth strategies have enabled the creation of novel one-dimensional morphologies that include nanotubes or tubular nanowires [16, 17], core–shell heterostructure nanowires [18, 19], and wires with different cross-sectional geometries [20, 21]. We review recently developed understanding and control of thermal phonon transport in a variety of these one-dimensional morphologies highlighting the basic physical principles that underlie thermal conduction process and the engineering of phonon transport in these structures. By elucidating different phonon engineering strategies, we aim to highlight the ability to create tailored thermal transport properties and heat conduction in semiconductor nanowires.

2. Thermal transport in nanowires

We start by introducing and analyzing heat conduction kinetic theory which constitutes the basis to understand many fundamental concepts of nanowire thermal transport. When a high temperature is applied to one end of a nanowire, the atoms at that end gain thermal energy and more lattice vibrations are created compared to atoms at the cold end. The net transport of these lattice vibrations along the axial direction of the nanowire—from the hot to the cold end—is the underlying physical mechanism behind heat conduction in semiconductor nanowires (figure 1). Quantized lattice vibrations are called ‘phonons’ and can be considered to be the particles of heat. Thermal conduction in semiconductor nanowires can thus be described as the *net transport of phonons* from the high temperature region to the low temperature region [22]. Phonons are characterized by their frequency ω of vibration, their propagation wavevector $\mathbf{k}$, and their longitudinal or transversal polarization. Phonons in solid materials can exist in a broadband range of frequencies ω determined by the dispersion relation $\omega(\mathbf{k})$, a fundamental material property giving the relation between the phonon frequency ω and the phonon wavevector $\mathbf{k}$ for each polarization. Being able to establish how much heat can be conducted in a solid material requires knowledge of three fundamental phonon transport properties—how much energy phonons can carry ($\hbar\omega_{\mathbf{k}}$), how fast they can move (group velocity $\mathbf{v}_{\mathbf{k}}$), and how far they can travel (mean free path $\ell_{\mathbf{k}}$). All these phonon transport properties contribute to the thermal conductivity κ of the material. Note that all these physical properties are dependent on the wavevector $\mathbf{k}$. In such kinetic theory description, the transport of heat under a thermal gradient is an aggregate behavior of phonons generated within the nanowire at each spatial location, moving along all directions with their wavevector dependent thermal transport properties $\hbar\omega_{\mathbf{k}}$, $\mathbf{v}_{\mathbf{k}}$, and $\ell_{\mathbf{k}}$, and their statistical average results in a net transport of thermal energy from the hot to the cold end of the nanowire, which is quantified by the thermal conductivity κ. The net heat flux $\mathbf{J}$ is given by $\mathbf{J} = -\kappa\nabla T$, where ∇T is the thermal gradient. Importantly, based on the above kinetic theory description, it is clear that the thermal conductivity κ can be manipulated by engineering the transport properties $\hbar\omega_{\mathbf{k}}$, $\mathbf{v}_{\mathbf{k}}$, and $\ell_{\mathbf{k}}$ of phonons in the nanowire.

We next provide insight on how the phonon transport properties can be affected and manipulated in bulk materials and nanowires. In bulk materials, heat carrying phonons are scattered via different processes that occur volumetrically also known as internal scattering processes. Internal scattering processes refers to the scattering of phonons by other phonons, electrons, holes, impurity atoms and isotopes of the constituent atom of the crystal lattice. In these scattering processes, the phonon momentum and thus its ability to carry heat is altered. Importantly, the strength of internal scattering processes determine the phonon mean free paths ℓ and thus the thermal conductivity κ of bulk materials since $\kappa \propto \ell$ [23, 24]. In nanowires, in addition to internal scattering processes, phonons can also be scattered by the nanowire boundaries (called as boundary scattering processes). Boundary scattering events arise when the phonon mean free paths are larger than the nanowire size and phonons can travel far enough to interact with the nanowire surfaces (figure 1). Note that while internal scattering is a volumetric scattering event, the boundary scattering of phonons is a discrete event occurring only at the surfaces. In a nanowire, the strength of both internal and boundary scattering processes determines the phonon mean free paths ℓ and the thermal conductivity κ of the nanowire. Due to the additional boundary scattering, the thermal conductivity of a nanowire is thus expected to be smaller than the corresponding bulk material. Manipulation of both internal scattering and boundary scattering processes on phonons lies at the heart of modulating thermal transport in nanowires. In the next section, we discuss in detail these two types of phonon scattering, that is, internal and boundary scattering.

2.1. Internal scattering in bulk materials

In this section, we consider isotopically pure bulk materials (no impurities) and discuss internal phonon–phonon scattering processes. In isotopically pure bulk materials, thermal transport can be understood as the diffusive transport of phonons internally scattered by other phonons [22]. The existence of phonon–phonon scattering poses a resistance to phonon transport and is the reason for finite values of phonon mean free paths ℓ and thermal conductivities κ in bulk materials [7]. During phonon–phonon scattering events, the energy is conserved while the wavevector $\mathbf{k}$ (or crystal momentum $\hbar\mathbf{k}$) may not be conserved. Phonon–phonon scattering processes that conserve momentum are called Normal processes and do not pose a resistance to thermal transport, while phonon–phonon scattering processes that do not conserve momentum are called Umklapp processes and are responsible for the resistance to thermal transport and finite thermal conductivities [7]. The rate at which phonon–phonon scattering processes occur is an intrinsic bulk material property that depends on many factors including the elastic constants, the atomic mass, and the phonon wavevector. Since phonons obey the Bose–Einstein statistics, the phonon–phonon scattering rate is also a function of the temperature since T controls the number of phonons (or phonon occupation numbers). At low temperatures very few states are occupied and the phonon–phonon scattering rate is very low due to the small number of phonons. In this case, the phonon mean free paths ℓ are relatively large and phonon transport is primarily controlled by phonon scattering processes occurring at the boundaries of the bulk material. In such a regime, the thermal conductivity follows the evolution of the material heat capacity C_v and scales proportional to T^3. At high temperatures, when nearly all phonon states are occupied, the phonon–phonon scattering rate becomes high due to the large number of phonons. In this case, the phonon mean free paths ℓ are relatively small and thermal conduction is primarily controlled by the phonon–phonon scattering rates. This leads to a reduction in thermal conductivity with increasing temperature that is proportional to $\sim 1/T$. For the purposes of thermal conductivity engineering, phonon–phonon scattering rates and thermal conductivities in pure bulk materials can thus be controlled by the temperature of the sample. Early studies on the thermal conductivity of bulk materials can be found in the works of Slack [23, 24].

2.2. Internal and boundary scattering in nanowires

Due to the presence of boundaries, in pure nanowires there exist boundary scattering of phonons in addition to internal phonon–phonon scattering. When phonons interact with the nanowire boundaries, a portion of them is scattered diffusely in all directions, leaving only the specularly reflected portion of phonons to continue to participate in the conduction of heat [7]. Diffuse phonon-boundary scattering processes pose a resistance to phonon transport and effectively shorten the phonon mean-free-paths ℓ in nanowires as compared to the mean-free-paths ℓ_0 in the bulk material. As a result, diffuse phonon-boundary scattering causes a strong reduction in the thermal conductivity κ of nanowires. Physically, κ decreases with reducing nanowire diameter since more phonons reach the boundaries and scatter diffusely thus reducing their ability to carry heat (figure 2(a)). The first formal understanding of the reduced transport of phonons by boundary scattering in nanowires stems from the electron transport models of Dingle [25], Chambers [26], and Sondheimer [27] which are based on the Boltzmann transport theory. These models allow for the quantitative evaluation of reduced mean free paths as a function of the surface specularity p, a quantity that represents the proportion of specularly reflected phonons on the nanowire surface. Walkauskas *et al* [28] applied these Boltzmann transport based models to predict the reduced thermal conductivity of GaAs nanowires with respect to bulk materials. Contemporaneously, Volz and Chen [29] showed that molecular dynamics can also be used to calculate the thermal conductivity of Si nanowires of very small diameters $d \sim 5$ nm. The first experimental verification of reduced thermal conductivities in nanowires was presented by Li *et al* [30] who showed that by reducing the diameters of vapor–liquid–solid (VLS) grown crystalline Si nanowires, a dramatic one order of magnitude reduction in thermal conductivities could be achieved. In particular, 30 nm diameter

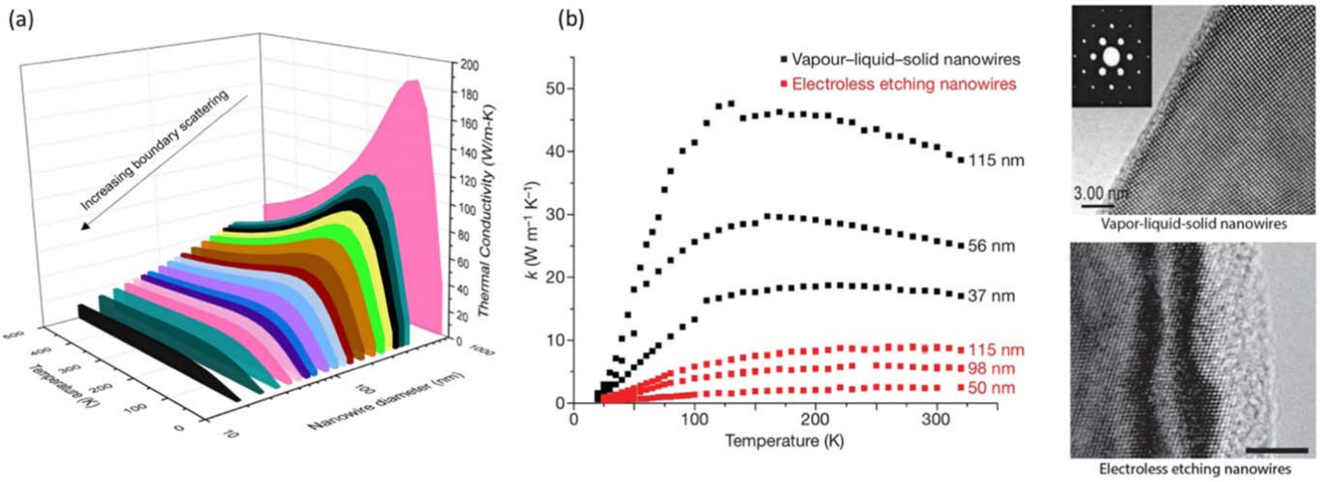

Figure 2. Role of boundary scattering in thermal transport. (a) Thermal conductivity calculations based on the Boltzmann transport equation as a function of nanowire diameter and temperature at constant surface roughness and correlation length. The thermal conductivity reduces with a reduction in nanowire diameter due to the increased number of phonon-boundary interactions. (b) Experimental evidence that increased boundary scattering can be achieved by either reducing nanowire diameters or increasing the surface roughness. Electroless etched nanowires (red squares) possess significantly higher surface roughness than VLS nanowires (black squares) and therefore a lower thermal conductivity. Measurements and TEM of etched nanowires (scale bar 4 nm) in panel (b) reprinted by permission from Macmillan Publishers Ltd: Nature research [8], Copyright (2008). VLS nanowire TEM (scale bar 3 nm) reprinted from [30], with the permission of AIP Publishing.

nanowires at $T = 300$ K showed $\kappa \sim 15\ \mathrm{W\,m^{-1}\,K^{-1}}$, a significant reduction from Si bulk values of $\kappa = 156\ \mathrm{W\,m^{-1}\,K^{-1}}$. These experimental findings were in agreement with theoretical understanding stemming from Boltzmann transport models showing that as the frequency of phonon-boundary interactions increased with reducing diameters, thermal transport is reduced in the nanowire. In their measurements Li *et al* noted that the thermal conductivity behavior of the thinnest 22 nm sample was distinct from the rest of the samples. The nanowire thermal conductivity at low temperatures (e.g. below 60 K for Si) is expected to scale with T^3 following the heat capacity because phonon–phonon scattering is diminished and temperature-independent boundary scattering dominates thermal transport [7]. However, it was found that while thick nanowires of diameter $d \sim 100$ nm followed the T^3 scaling of thermal conductivity, thin nanowires $d \sim 20$ nm deviated from this behavior and showed a scaling with T^1 which was speculated to arise due to quantum confinement effects. Quantum confinement is a phenomenon where a particle (e.g. electron or phonon) when confined spatially in a region, exhibits only certain allowed (quantized) states with modified density of states and group velocities. In the kinetic picture of phonon transport as detailed earlier, these modifications would change $\hbar\omega_{\mathbf{k}}$ and $\mathbf{v}_{\mathbf{k}}$. Models based on modified density of states and/or group velocities attempted to account for reduction in thermal conductivity by including these effects in addition to mean-free-path reduction due to diffuse scattering of phonons [31–33]. However, the modification of dispersion relations by quantum confinement requires the existence of sufficiently long mean-free-paths to create standing waves [34] which is hindered in the presence of a diffusive surface that shortens the mean-free-paths of phonons. Thus quantum confinement is expected to play a strong role only in thin nanowires ($d < 10$ nm) [35] with smooth surfaces especially at low temperatures [36], and therefore was an unlikely source of the observed reductions in thermal conductivity in the 22 nm nanowire of Li *et al*. More recently, experiments in top-down grown rectangular cross-sectional Si nanowires suggested that changes in thermal conductivity can be due to the reduction in the Young's modulus in large surface-to-volume nanostructures [37]. Similar findings have been reported in nanotubes with thickness less than 10 nm suggesting that modified mechanical properties (e.g. speed of sound) in low dimensional nanostructures could be a factor on thermal phonon transport [38]. A comprehensive understanding of thermal transport in sub-25 nm diameter nanowires continues to be an open question that requires additional studies.

After Li *et al* experimental demonstration of reduced thermal conductivity with reducing diameters, Hochbaum *et al* [8] further extended the idea of using boundary scattering to reduce thermal conductivity. The authors increased the roughness of the VLS grown Si nanowire surfaces with electroless etching in a solution of $AgNO_3$ and HF (figure 2(b)). The thermal conductivity of these intentionally roughened nanowires was found to be almost one order of magnitude smaller compared to nanowires of similar diameters in the work of Li *et al*. The strong reduction in thermal conductivity stems from the increased diffuse surface scattering of phonons in these rough nanowires severely limiting their mean-free-paths. While initial models claimed an excellent agreement with these measurements by considering an interfacial roughness of 3 nm [39], the models were double counting the impact of surfaces [40]. In general, theoretical predictions for roughened nanowires are higher than the measured thermal conductivities, which could be due to by the existence of the oxide layer at the nanowire surface [41, 42] and possibly due to the existence of defects in the

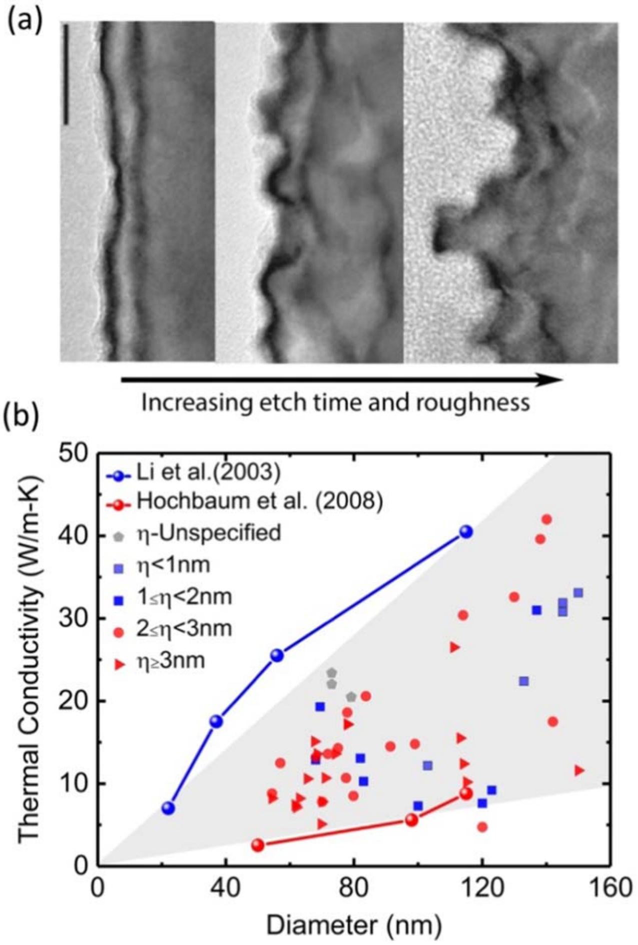

Figure 3. (a) Etching conditions can be used to control surface properties and engineer nanowires with desired thermal properties. Scale bar in the upper left corner is 10 nm. (b) Current state of room temperature thermal conductivity engineering of nanowires. Thermal conductivity measurements by Li *et al* on VLS nanowires [30] and Hochbaum *et al* [8] on electroless etched nanowires form an envelope around all other measurements, indicative of an experimental bound on thermal conductivity. Panel (a) reprinted from [46], with the permission of AIP Publishing.

nanowire core [41], which can reduce the thermal conductivity in the experimental samples. Subsequent measurements of etched nanowires with similar diameters exhibited higher thermal conductivities (figure 3(b)) supporting this hypothesis experimentally, as quantitative agreement between experiments for similar diameter and surface roughness continues to evolve. In addition to the surface roughness, a quantitative description of nanowire surfaces requires the knowledge of the surface correlation length. Taking the example of a simple sinusoidal surface profile, the surface roughness and correlation length provides the information about the amplitude and the periodicity of the profile, respectively. Recent experimental studies found that thermal conductivities in nanowires are related to both the roughness and the correlation length of the nanowire surface [43]. Thus, in order to fully describe thermal transport, both surface roughness and correlation lengths for nanowires are now characterized and reported [44–46]. Despite these recent experimental advances, theoretical studies that can predict thermal transport using quantifiable surface parameters in realistic nanowires are currently limited. For example, to evaluate the impact of boundary scattering, theoretical approaches were introduced where boundary scattering and internal phonon scattering rates are combined to obtain an effective phonon relaxation time (known as the Matthiessen's' rule) [7]. The fundamental drawback of these formulations is that they combine the volumetric scattering (phonon–phonon) events with discrete surface scattering (phonon-boundary) events as if they are both volumetric. In this regard, solution methodologies to the Boltzmann transport equation have been implemented to preserve the discrete nature of phonon-boundary scattering while including surface roughness [47, 48]. Sampling based simulations such as Monte Carlo techniques are inherently equipped to handle the discrete nature of interactions between phonons and nanowire boundaries, but the rigorous incorporation of surface properties and its impact on thermal transport in this technique remains limited. In particular, the inclusion of surface roughness, correlation length, and incident angle dependent phonon scattering at nanowire surfaces are key aspects of accurately predicting thermal transport in nanowires. Recent computationally efficient studies on nanowires based on the Boltzmann transport equation have allowed for incorporating surface roughness and correlation lengths to include incident angle dependent phonon scattering phenomenon using Beckmann–Kirchhoff scattering theory for undulating surfaces [47, 49], allowing for inclusion of quantifiable surface descriptors in predictive models for thermal transport that can be compared to realistic experimentally growth nanowires.

We note that the majority of the thermal conductivity modifications in nanowires, especially in experimental nanostructures, can be understood by the presence of internal phonon–phonon scattering in addition to phonon-boundary scattering. In such cases, the mean-free-paths of phonons are shortened and the thermal conductivity reduced with respect to bulk due to the diffuse (incoherent) scattering of phonons at the nanowire boundaries. We also note that there may also exist certain phonon interference phenomena that can arise when phonons preserve their phase upon specular scattering with nanowire surfaces, termed as coherent effects, which lead to modulations in phonon dispersion relations and change in phonon group velocities and density of states [34, 50]. In the rest of this paper, we focus our discussion in exploring the possibilities for engineering incoherent and coherent phonon-surface scattering and thermal transport as well as other recently developed mechanisms to modulate nanowire thermal conduction that build upon the fundamental developments discussed in this section.

3. Leveraging internal phonon scattering

In addition to phonon–phonon scattering, phonons can be internally scattered by impurities in the crystal lattice. The presence of atoms of a different mass and radius in the crystal lattice acts as scattering centers for phonons, which increases

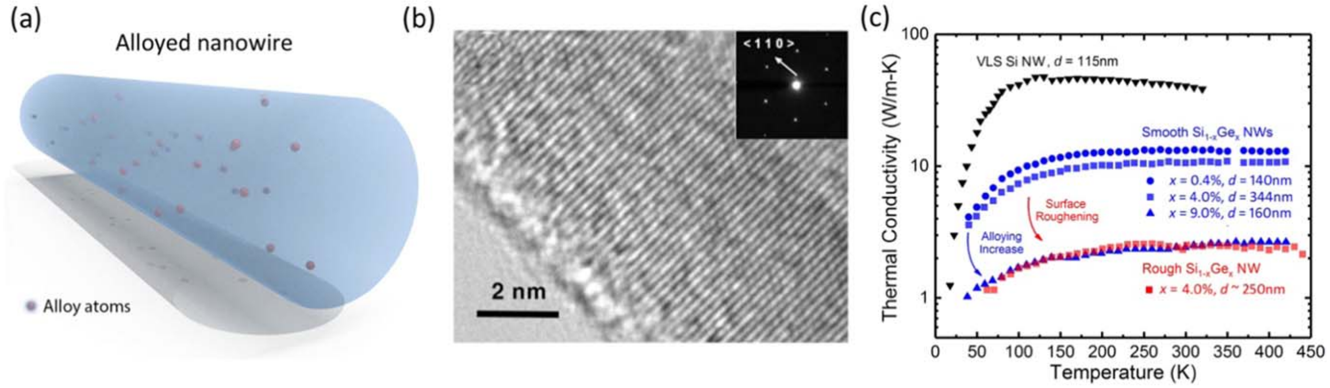

Figure 4. Thermal transport in alloyed nanowires. (a) Schematic showing a crystalline nanowire with alloy atoms at random spatial locations, which act as scattering centers for phonons. (b) TEM image of a Ge alloyed Si nanowire showing the crystalline and defect-free nature of growth. Inset shows a diffraction pattern along the growth direction $\langle 110\rangle$. (c) Thermal conductivity measurements of alloyed nanowires (blue and red colors) shown along with a pure Si nanowire of diameter $d = 115$ nm (black). Increasing alloying for smooth nanowires (blue) reduces the thermal conductivity to a threshold, which can also be achieved by roughening of alloyed nanowires (red square). Panel (b) reprinted from [60], with the permission of AIP Publishing.

the overall internal scattering rates of phonons and can additionally reduce the phonon mean free paths. These atoms could be the naturally occurring isotopes of the elements or impurity atoms in the host crystalline lattice. The scattering of phonons by internal impurities has implications not only on the resultant thermal conductivity of the nanowire but also on the specific phonon frequencies that dominate thermal conduction. In this section, we discuss both these aspects and describe the recent progress on the use of internal scattering mechanisms to modulate thermal conduction.

3.1. Mass-difference scattering

Elements on Earth are mostly found as a mixture of isotopes, some of which have short lifetimes due to an unstable nucleus [51]. For instance, natural silicon occurs as a mixture of three stable isotopes ^{28}Si, ^{29}Si and ^{30}Si with approximately 92.3%, 4.7%, and 3% abundance [52]. Thus, any nanostructure made with natural Si would exhibit relative difference in the mass of Si atoms in the lattice. For thermal phonons, an isotopic atom with mass different than most atoms in the lattice acts as a scattering center, leading to reduced mean free paths and thus lower thermal conductivities in natural silicon than in isotopically enriched silicon [53]. Theoretical [54] and experimental [55] approaches have exploited the mass-difference arising from isotopes and the consequent phonon-impurity scattering to engineer reduced thermal conductivities in nanostructures. However, a more experimentally realizable approach to leverage mass-difference scattering to modulate heat conduction involves the use of alloying atoms. The presence of alloy atoms having different mass within a crystal lattice creates scattering centers for phonons (figures 4(a), (b)) (especially for phonons with high frequencies) and reduces the thermal conductivity. Studies on bulk SiGe alloys showed that most of the reduction in thermal conductivity occurs at small mass fractions of Ge and saturates as the alloying fraction is increased above ~10% [56–58]. In the case of nanowires, Chen *et al* [59] showed using molecular dynamics simulations that alloying of Si nanowires with a few percent of Ge atoms is actually sufficient to lead to a strong reduction (~50%) in thermal conductivity as compared to pure Si nanowires. This study, however, was focused on nanowires with very small diameters ($d \sim 2$ nm). Experimentally, Kim *et al* [60] measured the thermal conductivity for a wide array of nanowire diameters ($d = 140$–344 nm) (figure 4(c)) and found that alloyed Si nanowires grown via the VLS technique can possess thermal conductivities an order of magnitude lower than pure Si nanowires. The impact of alloying on thermal conductivity has been explored across a wide range of alloying fractions [61–63]. The first connection between experiments and theory came with the Boltzmann transport based model of Wang *et al* [64] who showed that accounting for phonon-alloy and phonon-boundary scattering mechanisms allowed for an excellent agreement with the experimental measurements. Further advances in theoretical approaches have enabled a better understanding of thermal transport in these nanowires, including the presence of anisotropy [65] as well as the dependence of thermal conductivity with reduced diameter owing to scattering of high frequency phonons by alloying [36]. Furthermore, since this reduction in thermal conductivity is not linearly correlated with changes in electrical conductivity, it can lead to a high thermoelectric efficiency in these nanostructures which requires a low thermal conductivity while maintaining a high electrical conductivity [66].

In addition to reducing the thermal conductivities of nanowires, alloying can alter thermal transport in another way viz. by modifying the amount of heat carried by phonons with different thermal properties (i.e. phononic heat spectra). Specifically, heat spectra refers to the relative contributions of a particular phonon frequency, wavelength, or mean-free-path to the overall thermal transport process in a nanowire [36]. The scattering of phonons from alloy atoms can be understood as the Rayleigh scattering of sound waves from a rigid sphere with different mechanical properties, making the phonon-alloy scattering rate a strong function of phonon frequency ($\sim 1/\omega^4$) [7]. Thus, phonons of high frequencies (short-wavelengths, small mean-free-paths) would be strongly scattered by alloy atoms, while low frequency (long-wavelength, large mean-free-paths) phonons remain relatively unperturbed by the presence of alloy atoms. For example, this frequency selective scattering causes a 'red-shift' of thermal transport towards low frequency phonons in the case of Ge alloyed Si nanowires as compared to pure Si nanowires [36]. The red-shift of thermal phonon frequencies with the use of alloys can be leveraged to create thermocrystals, a nanostructure in which heat is carried primarily by low frequency large-wavelength phonons allowing it to be coherently modified by periodic nanostructuring [67]. For SiGe alloy nanowires with surface roughness of $\eta = 0.5\,\mathrm{nm}$, theoretical predictions on the proportion of heat conducted by phonons with mean-free-paths $\ell > 1\,\mu\mathrm{m}$ have been estimated to be $\sim$20% [36]. For smoother nanowires, calculations showed that more than 50% of the heat is carried by phonons with mean-free-paths in the range $\ell > 1\,\mu\mathrm{m}$ at room temperature. Similarly, Monte Carlo simulations [68] have also estimated that phonons between $\ell \sim 1{-}10\,\mu\mathrm{m}$ would account for $\sim$50% of heat conduction. These theoretical results show that phonons with mean-free-paths larger than $1\,\mu\mathrm{m}$ contribute significantly to thermal transport. While the exact quantification of the contribution of phonons with large mean-free-paths to thermal transport in SiGe nanowires remains to be validated experimentally, the modification of phonon transport properties (e.g. frequency, mean free path) arising from phonon-alloy scattering is a valuable tool to rationally design thermal conduction in nanowires.

In addition to point impurities such as alloying atoms, the use of clusters of atoms (i.e. Ge nanoparticles) has also been considered to reduce thermal transport and create efficient bulk thermoelectric materials [69]. The larger size of impurity nanoparticles allows for a different range of phonons to be scattered as compared to point alloy atoms. It has also been shown that under the constraint of constant total impurity percentage, an optimal diameter distribution of nanoparticles can be obtained to maximize the reduction in thermal conductivity [70]. In the case of nanowires, it was found experimentally that by placing Ge nanoparticles on a silicon nanowire, thermal conductivity can be reduced by 23% [71]. Thus, the use of impurity atoms whether individually or as clusters signifies the opportunities for engineering thermal conduction by manipulation different phonon scatterings and transport in nanowires.

3.2. Phonon-charge carrier scattering

Since electronic applications of silicon require creation of free-charge carriers in the form of electrons and holes created via doping, studies on doped silicon nanowires have focused primarily on the electronic properties [72–74] and thermal properties of doped silicon nanowires are less understood. In general, thermal conductivity of doped silicon can be expected to be lower than its undoped counterpart for two reasons. First, phonons can scatter from dopant atoms as they are distinct from the atoms of the lattice, and second, phonons can interact with the free-carriers generated by these dopants. From a physical perspective, the large difference in masses of nuclei and electrons allows for independent treatment of either, referred to as the Born–Oppenheimer approximation. Thus, phonons being the motion of the heavier nuclei of atoms are assumed to interact weakly with electrons. Experimental studies on bulk silicon and silicon thin films have confirmed these expectations, showing that under dopant concentrations less than $10^{16}\,\mathrm{cm}^{-3}$, thermal conductivity is weakly perturbed by phonon interactions with carriers especially at room temperatures [75, 76]. Recent advances in first-principle calculations using density functional theory (DFT) have also confirmed that impact of doping on thermal transport is expected to be strong only at high dopant concentrations ($>10^{19}\,\mathrm{cm}^{-3}$) [77]. In nanowires, a combination of dopant concentration and diameter design has been used to obtain high thermoelectric efficiency by obtaining relatively large electrical conductivities and small thermal conductivities [78]. DFT calculations for Si nanowires have also shown that doping (n-type or p-type) coupled with crystal growth direction can be used as a design variable in engineering thermal conductivities at large dopant concentrations [79]. To experimentally obtain such doped nanowires, reactant flow during the VLS growth is changed to include dopant atoms [72]. Another approach involves embedding dopant atoms after growth using ion beams [80], which we will discuss in more detail next. In either methodology, the central principle is the same, addition of dopant atoms creates more electrons or holes in the nanowire, which for large dopant concentrations will enhance the phonon scattering from these extra carriers and thus reduce the nanowire thermal conductivity.

3.3. Amorphous scattering

Another interesting idea to control nanowire heat conduction involves the modification of phonon transport post nanowire growth by controlled amorphization of the nanowire. Instead of modifying standard VLS growth process as was the case for embedding alloy atoms, a downstream ion beam bombardment unit operation can be added or removed at will depending on the desired thermal properties of grown nanowires. The separation of the two processes—growth and structural modification—is an attractive proposition from a large scale manufacturing perspective as it enables easier process troubleshooting and maintenance. If a highly energetic beam or a beam of heavier atoms is used to bombard the nanowire, the crystalline structure of nanowires can effectively be damaged locally to engineer disorder. Such engineered disorder sites then act as scattering centers for phonons. In an effort to engineer disorder, a 30 kV Ga^{+} ion beam was used on a Si nanowire to create a region of disorder while maintaining the crystallinity of the wire, following which the measured thermal conductivity was strongly reduced [81]. Similarly, bombardment with lighter He ions was explored to create scattering centers with uniform spatial distribution throughout the wire [82]. Interestingly, the effect of ion bombardment has been found to be reversible to a large extent, and with the use of high temperatures the created point

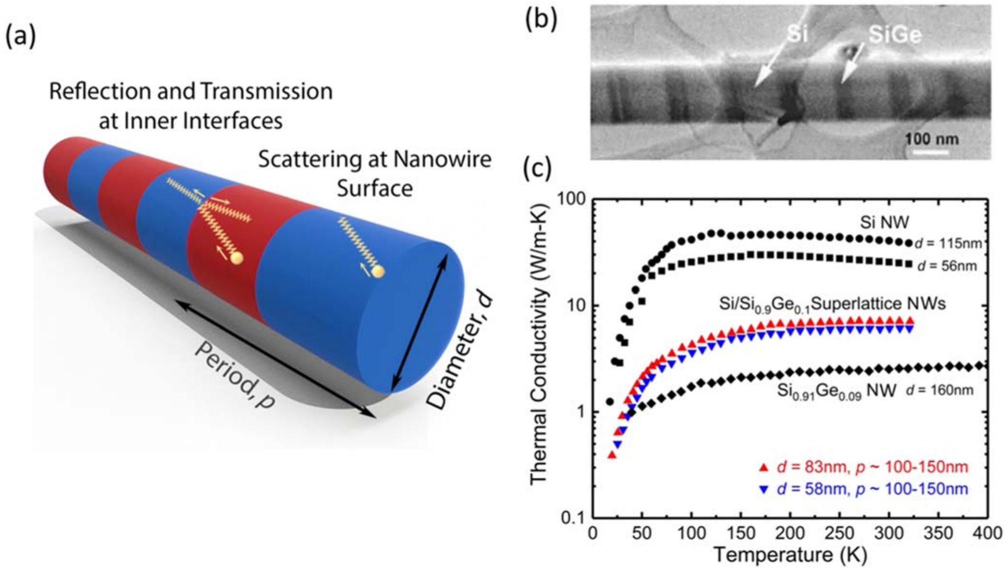

Figure 5. Superlattice nanowires. (a) A schematic depicting the structural parameters of superlattice nanowires, the period *p* and the diameter *d*. In addition to scattering at the nanowire surface, phonons can be reflected and transmitted at the inner interfaces in a superlattice nanowire. (b) A TEM image of Si/SiGe superlattice nanowire showing the internal interfaces. (c) Thermal conductivity measurements of $Si/Si_{0.9}Ge_{0.1}$ nanowires across a range of temperatures showing that their thermal conductivity lies between pure Si and ~10% Ge alloyed Si nanowires. Panel (b) reprinted from [84], with the permission of AIP Publishing.

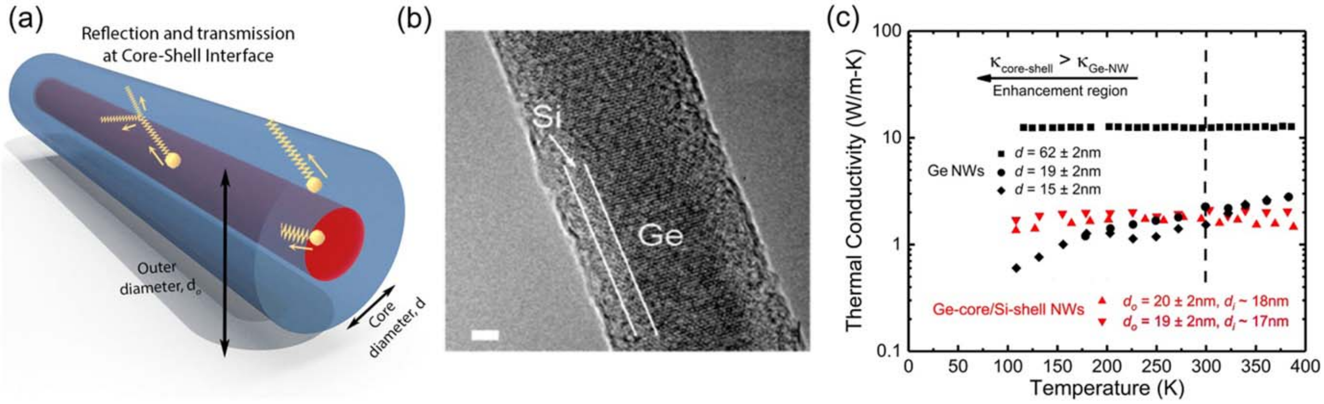

Figure 6. Core–shell heterostructure. (a) Core–shell nanowires possess two interfaces specified by diameters, inner d_i and outer d_o and phonons can scatter at both these interfaces. Note that phonons can reflect and transmit at the inner interface. (b) A TEM image of Ge core Si-shell heterostructure nanowire. Scale bar is 2 nm. (c) Thermal conductivity measurements of core–shell nanowires (red) compared with Ge nanowires (black) of similar diameters. Above room temperatures measurements indicate that core–shell nanowires have a lower thermal conductivity than pure Ge nanowires while the behavior is inverted at lower temperatures. Ge nanowire with larger diameter $d = 62$ nm showed negligible dependence on temperature. Panel (b) reprinted with permission from [96]. Copyright 2011 American Chemical Society.

defects can be thermally annealed. Further understanding and research into engineered disorder could be important as tools for rationally controlling thermal transport in nanowires. The strong impact on phonon scattering by a disorder crystal coupled with phonon-boundary scattering is an exciting pathway towards modulating the transport of heat in semiconductor nanowires.

4. Heterogeneous nanowires: the impact of internal surface scattering

The use of interfaces to control heat conduction can be extended beyond phonon scattering at nanowire boundaries by considering heterogeneous nanowire structures. In heterogeneous nanowires, different constituent materials can be arranged axially or radially and the interfaces separating the materials are additional sources of phonon scattering. For example, in periodic structures such as superlattice nanowires, multiple material interfaces are perpendicular to the nanowire axis (figure 5(a)), while in core–shell nanowires material interfaces are arranged in the radial direction (figure 6(a)). In heterogeneous nanowires, the presence of different materials across the interfaces allows for the reflection and transmission of phonons at the interfaces creating novel phonon-surface interactions that can be used to engineer thermal transport.

The reduction in the thermal conductivity of superlattice nanowires has been investigated for different material systems, e.g. Si/Ge and PbTe/PbSe [83, 84]. Superlattice nanowires are grown using approaches that require changing the reactant gas in the VLS growth process as a function of time coupled with close control over growth conditions [85, 86]. Measurements of thermal conductivity in Si/SiGe superlattice nanowires suggested that the thermal conductivity was significantly suppressed due to diffuse scattering of phonons at material interfaces as well as diffuse alloy scattering of phonons within the SiGe material layer [84]. For Si/Ge superlattice nanowires, theoretical predictions for nanowires with diameter $d \sim 20\,\mathrm{nm}$ and period $p < 100\,\mathrm{nm}$ indicated that thermal transport could significantly be suppressed even below the alloy thermal conductivity [87]. However, experimental measurements for nanowires with $d = 58\,\mathrm{nm}$ and $d = 83\,\mathrm{nm}$, period $p \sim 150\,\mathrm{nm}$ showed that the thermal conductivity of these wires was between the conductivity of a pure Si nanowire and a Ge alloyed silicon nanowire (figure 5(c)) [84]. Significantly, a theoretical investigation into PbSe/PbS and PbTe/PbSe superlattice nanowires found that thermal conductivity reduction was stronger than the reduction in electronic transport, showing the potential of superlattice nanowires for thermoelectric applications [83].

Theoretical approaches for superlattice nanowires treat, in general, thermal phonon transport as incoherent, where only the effects of diffuse scattering of phonons at interfaces are considered. A superlattice nanowire with periodically arranged smooth interfaces allows for phonons to specularly reflect and transmit from multiple interfaces. Under certain conditions, phonon specular reflection and transmission can result in the coherent interference of phonons, which can open up forbidden frequency zones known as bandgaps, implying that phonons with certain frequencies cannot travel in the structure [50]. Importantly, coherent interference of thermal phonons can also create a minimal thermal conductivity for a specific superlattice period [88]. To observe phonon coherent interference, it is required that phonons cross multiple interfaces while maintaining their phase, meaning that smooth interfaces (in contrast to rough surfaces) are favorable for the development of coherent thermal transport. Using molecular dynamics, theoretical studies on the impact of coherent interference of phonons in superlattice nanowires have been introduced, showing the existence of a minimal thermal conductivity for a specific lattice period [89, 90]. These studies, however, have been focused on very thin nanowires with perfect surfaces, which are difficult to realize experimentally. In thin-film superlattices, a minimum in thermal conductivity [88] with decreasing period has been theoretically analyzed in Si/Ge superlattices [91] and experimentally observed in $SrTiO_3/CaTiO_3$, $SrTiO_3/BaTiO_3$, TiN/AlN and TiN/ScN superlattices indicating the existence of coherent thermal phonon transport [92, 93]. Central to the development of coherent transport is the existence of smooth interfaces, since rough surfaces remove the signature of coherent thermal transport, making the thermal conductivity to reduce monotonically with decreasing period (i.e. no minimum) [94]. In superlattice nanowires, the stronger surface scattering as compared to thin-film superlattices (due to nanowire boundaries) constitutes additional scattering for phonons, which could impact the observation of coherent interference. Thus, the key strategies to experimentally validate coherent thermal transport in superlattice nanowires would involve the use of smooth surfaces (e.g. lattice-matched materials) to minimize diffuse phonon-surface scattering both at the nanowire boundaries and the material interfaces.

Another heterogeneous nanowire structures where phonons can reflect and transmit across interfaces between different materials are core–shell nanowires. Unlike superlattice nanowires, where the interfaces between materials are normal to the nanowire axis, in core–shell nanowires the interfaces are in the radial direction (figure 6). Standard growth techniques for core–shell nanowires require radial control [18, 95] and rely on growth of the core nanowire on a gold catalyst using the VLS mechanism, followed by changing growth conditions to favor homogenous vapor phase deposition on the nanowire surface. Recent developments in metrology of these structures have revealed that thermal conductivity in Ge–Si core–shell nanowires above room temperature is lower than Ge nanowires of similar diameters (see figure 6(c)) [96]. Thermal and electrical measurements also suggest that these core–shell nanowires could be engineered to have higher thermoelectric efficiencies than bulk Ge [97]. One of the reasons for the suppression in thermal conductivities of core–shell nanowires is the diffuse scattering of phonons at the interface of the core and shell layers [98]. Molecular dynamics simulations found that the vibrational density of states in the core–shell nanowires can be modified, reducing the thermal conductivity [99, 100]. For Si–Ge core–shell nanowires with a Si-core of $2.3\,\mathrm{nm} \times 2.3\,\mathrm{nm}$ square cross-section, the thermal conductivity was found to lie in the range of $3\text{–}9\,\mathrm{W\,m^{-1}\,K^{-1}}$ depending on the Ge shell thickness. Even though both experimental measurements and theoretical models qualitatively seem to agree that thermal conductivity in core–shell nanowires is reduced with respect to nanowires, experimental measurements have found a unique region at less than 300 K in Ge–Si core–shell nanowires where thermal conductivity is enhanced above Ge nanowires with similar external diameters (figure 6(c)) [96], warranting further investigations on the role of surface scattering on thermal transport in core–shell nanowires.

5. Novel structuring of nanowires

5.1. Surface modulated nanowires

With recent advances in nanostructuring fabrication methods, nanowires with varying cross-section along the nanowire length have recently been grown with the use of electron beam lithography (figure 7) [101]. An example of modulated diameter nanowires are corrugated nanowires in which the diameter is continuously varied creating a sinusoidal-like periodic boundary profile. Thermal conductance measurements in these corrugated nanowires with $\sim 200\,\mathrm{nm} \times 200\,\mathrm{nm}$ cross-section at very low temperatures ($T < 10\,\mathrm{K}$) showed that the mean-free-paths of phonons are reduced by a

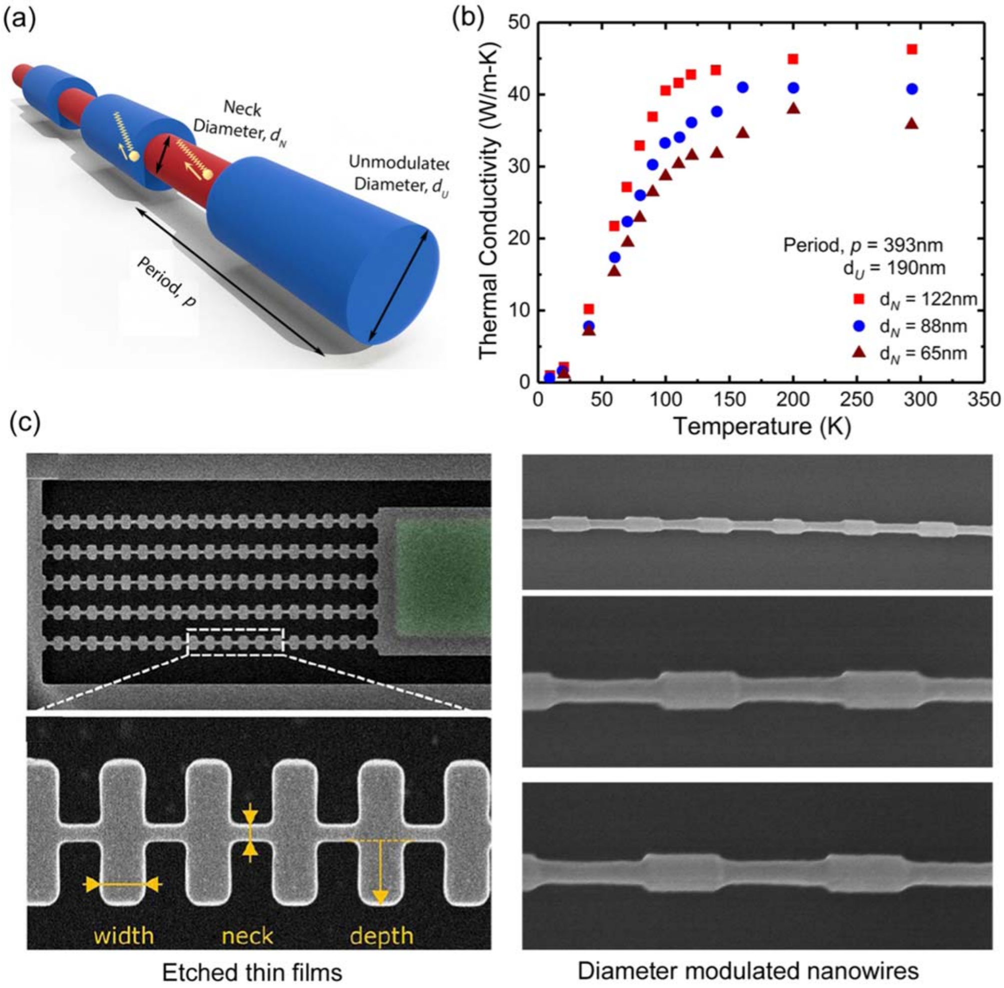

Figure 7. Modulated diameter nanowires. (a) A schematic showing the structure of a modulated diameter nanowire specified by the neck diameter d_N and the unmodulated diameter d_U. (b) Thermal conductivity measurements show that reducing neck diameter inhibits the transport of phonons, lowering the thermal conductivity. (c) These structures can be created from top-down approach by etching thin films or with a bottom-up growth of modulated doped nanowires followed by selective etching. Etched thin films panel reproduced from [101]. CC BY 4.0. Diameter modulated nanowires panel from [130].

factor of eight compared to the mean-free-paths in straight nanowires, creating a strong reduction in thermal transport [102]. Another modulation profile consists of a change in cross-sectional dimensions alternating between large and small cross-sectional square nanowires. In such step modulated nanowires, recent experimental measurements found that thermal conductivity is strongly determined by the size of the smaller nanowire section (i.e. neck) (figure 7(a)) [101]. For instance, at room temperatures, the thermal conductivity of modulated nanowires was reduced from $\kappa \sim 45$ to $\kappa \sim 28\ \mathrm{W\,m^{-1}\,K^{-1}}$ upon reducing the neck size from 122 to 45 nm. It was also observed that by increasing the difference between the smaller and larger cross-sectional dimension, a small reduction in thermal conductivities was obtained which was not predicted by phonon transport simulations [101]. At very small length scales, molecular dynamics simulations have suggested that by engineering modulations in nanowires of diameter $d \sim 5$ nm, strong reduction in thermal conductivity can be obtained due to the changes in the phonon dispersion relations caused by acoustic softening [103], which reduces the phonon velocities in nanostructures. Solution to the Boltzmann transport equation coupled with lattice dynamics calculations for thin nanowires have also proposed similar modification to phonon dispersion relations and consequentially thermal conductivities [104]. These results suggest that additional physical mechanisms beyond diffuse phonon scattering from rough surfaces could be an exciting area for both theoretical and experimental research at very small diameter nanowires.

5.2. Nanotubes

Tubular semiconductor nanowires or nanotubes are structures similar to core–shell nanowires where the core is devoid of solid material and filled with air. The origin of the terminology can be traced back to carbon nanotubes which consisted of a graphite sheet rolled into a cylinder [105]. Such carbon nanotubes were found to possess high thermal conductivity as phonons in graphene could travel for large distances without significant scattering [106]. The external and internal surfaces of a hollow silicon nanowire (or silicon nanotube) however cause phonons to scatter more than those in standard nanowires, and are therefore to generate reduced thermal conductivities. Experimentally, silicon nanotubes can be prepared by growing a Ge–Si core–shell nanowire, followed by etching away the Ge core using peroxide solutions to leave behind the hollow Si shell [107]. The methodology was employed to grow hollow crystalline and amorphous Si nanotubes with shell thicknesses $t \sim 5\text{–}10\,\text{nm}$ and outer diameters greater than $d = 40\,\text{nm}$ [38]. Surprisingly, the thermal conductivity of crystalline nanotubes was measured to be $\kappa \sim 1\,\text{W m}^{-1}\,\text{K}^{-1}$ at room temperature even smaller than amorphous nanotubes ($\kappa \sim 1.5\,\text{W m}^{-1}\,\text{K}^{-1}$), and was attributed to the reduction in group velocities due to material softening arising from the reduced length scale of the shell thicknesses (in addition to diffuse surface scattering). Such softening of phonon modes has also been observed in very thin Si nanoribbons with high surface-to-volume ratios [37]. In these thin nanostructures, the surface atoms play a strong role and their lowered coordination numbers in comparison to atoms in the interior could be a reason for reduced phonon velocities. The existence of amorphous oxide layers around the nanotube shells also plays a role in impacting thermal transport as will be discussed later in section 5. Molecular dynamics calculations for nanotubes have suggested that a small hollow core corresponding to 1% reduction in the nanowire of cross-sectional area of $\sim 5\,\text{nm}^2$, creates a reduction in thermal conductivity by one-third from $\kappa = 12$ to $\kappa = 8.8\,\text{W m}^{-1}\,\text{K}^{-1}$ [108]. Boltzmann transport based model for nanotubes considering experimentally achievable nanowire diameters have recently shown quantitatively that the evolution of the thermal conductivity with changing outer diameter is a strong function of interface conditions at both the inner and outer interface [109]. It is important to note that while the minimum diameter of VLS grown nanowires is determined by the gold catalyst size, the nanotube growth strategy via etching allows for studying nanostructures with characteristic sizes less than 25 nm. Thus, investigations of modified elastic properties, role of amorphous oxide layer, and role of structural properties including inner and outer diameters as well as interfacial conditions at these boundaries would help fill the gaps in the current understanding of nanoscale thermal transport in very thin nanowires.

5.3. Embedded pores

A novel idea on the use of phonon-surface scattering to control thermal conduction involves embedding surfaces inside a nanowire by means of nanopores. Experimentally, nanowire arrays with embedded pores as well as individual nanowires have been produced by metal assisted chemical etching [110, 111]. In nanoporous nanowires, the embedded pore surfaces provide an additional source for phonon scattering, which strongly reduces the mean-free-path and the nanowire thermal conductivity as compared to nanowires without embedded pores. In addition, the increasing porosity further reduces the thermal conductivity by introducing a larger fraction of low thermal conductivity phase (air). The degree of porosity is a tunable physical variable that can be exploited to control the thermal conductivity since a higher porosity would create more frequent scattering of phonons at the nanopore surfaces (and also add more low thermal conductivity phase). It has been shown that porosity can be controlled experimentally by a variety of experimental parameters including the resistivity of the starting silicon wafer, the concentration of dopant atoms, the concentration of peroxide as oxidant, and the amount of catalyst [110]. Measurement of thermal conductivity in nanoporous nanowires have validated that thermal conductivities are in general reduced with increased porosity [112, 113]. For example, by using different doping concentration in silicon nanowire arrays, metal assisted chemical etching technique was used to produce nanowires of varying porosities [113]. In addition to modulating doping concentration, chemically changing etch conditions are another way to create structures with high porosity. For instance, for nanowires with diameter $d = 130\,\text{nm}$, the thermal conductivity is reduced from $\kappa = 38$ to $\kappa = 17\,\text{W m}^{-1}\,\text{K}^{-1}$ when etchant peroxide concentration was increased from 0.15 to 1.2 M [113]. In contrast, the electronic transport is not impacted by the porosity to the same degree, which increases the thermoelectric efficiency in these nanowires [112]. Apart from modulating thermal conductivity making them useful in thermoelectrics, nanoporous nanowires have other interesting applications in optoelectronics, supercapacitors, and drug-delivery [114]. All of these applications arise from their tunable physical properties and most importantly due to their large surface area to volume ratios.

5.4. Surface chemistry

In addition to controlling the surface roughness of the nanowire boundaries, surface chemistry provides another mechanism to engineer phonon scattering at the boundaries and control the thermal conductivity of nanowires [115]. It was observed that HF etching followed by surface hydrogenation could provide nanowires with higher thermoelectric efficiency due to reduced thermal conductivities via boundary impurities [116]. From a theoretical point of view, it has also been postulated that surface nitrogenation can reduce the thermal conductivity strongly as compared to a pure silicon nanowire [117]. The reasons for such reduction have been attributed to defect creation closer to the surfaces with nitrogenation as well as the modification of phonon density of states that arises due to mass-difference between silicon and nitrogen atoms. In other words, certain thermal vibrations are hindered because of difference in atomic masses at the interface. Other heavy functional groups such as alkyls are also expected to produce similar effects [118]. Apart from the engineered functionalization of the surfaces, the growth of nanowires is often accompanied with a native oxide layer on the surface—in particular for the case of silicon. This native amorphous silicon oxide can be understood as the addition of a new material shell around the crystalline silicon nanowire. Molecular dynamics calculations showed that the transport dynamics in such an amorphous shell can be significantly reduced in contrast to a crystalline wire. For very thin nanowires ($d < 3\,\text{nm}$), calculations found that thermal conductivity in amorphous shell nanowires was independent of temperature, indicating that the temperature dependent phonon–phonon scattering mechanism does not play a determining role [119]. The difference in thermal transport between crystalline and amorphous shell nanowires is postulated to arise from the transformation of propagating phonon modes to diffusive modes at room temperature. On the other hand, findings on thin nanotubes have suggested that thermal conductivity of amorphous nanotubes can be larger than those of crystalline nanotubes [38]. We note that even outside the domain of nanowires, the exact nature and contribution of different vibrational modes to thermal transport in amorphous silicon remains an open debate [120–123]. From an experimental perspective, it is hard to design experiments to discern the role of amorphous surfaces on thermal transport since native oxide is a standard feature of nanowire growth. Studies in nanomeshes (i.e. structures made of periodic arrays of air pores in thin films) have shown that accounting for amorphous regions is critical to ensure a fundamental basis of comparison between theory and measurements [124]. Further experimental validations in nanowires could help bring a detailed understanding on the role of amorphous surfaces on thermal transport that is currently lacking.

6. Conclusions and perspectives

Recent developments in nanowire fabrication techniques and thermal conductivity measurements have fueled fundamental understanding of thermal phonon transport in low dimensional systems. As shown in this review, most work on modifying thermal phonon transport in semiconductor nanowires have relied on the basic physical principle of manipulating the phonon mean-free-paths. We showed that such control of phonon mean free paths has been experimentally achieved by modulating the internal phonon scattering rates (e.g. phonon–phonon, phonon-impurity scattering) as well as controlling the scattering of phonons with nanowire interfaces and boundaries. This strategy has resulted in the development of multiple one-dimensional nanostructures with specific tailored thermal conductivities, including alloyed and rough-surface nanowires, superlattice nanowires, core–shell nanowires, nanotubes, and cross-section modulated nanowires.

There are several important open questions both practical and fundamental, which need to be addressed to further advance our understanding of heat transport in nanowires and create functional devices for technological applications. Clearly, one key issue for translation of fundamental development to application scale is the creation of abilities for large scale fabrications consistent with nanowire morphologies. Another key point in nanowire heat conduction research is the ability to provide samples and experimental measurements that can be consistently repeated. Note that nanowire diameters and surface conditions are central to their resultant thermal transport properties. In addition, the presence of a few percent of impurities is sufficient to strongly change phonon transport characteristics in these structures making consistency within and across batches a central focus of research. Furthermore, in a large scale setup both high throughput fabrication as well as high throughput measurement techniques would need to be developed to ensure quality control. Other factors such as cost of raw materials, environmental and health safety, as well as the ability to automate the developed processes would need to be considered to create a larger scale setup that can leverage the developments in fundamental understanding of thermal transport at the nanoscale.

An important development that has not yet been explored is the ability to enhance nanoscale thermal transport. In general, surfaces have been used to shorten the phononic mean-free-paths via diffuse scattering, restricting the use of nanowires to obtain low thermal conductivities. In order to achieve a more complete material design paradigm, it would be central to develop the capability to fully tune the thermal conductivity, e.g. increase the mean-free-paths to obtain desired values of thermal conductivity. Such approaches have been initiated for layered nanomaterials where both increase in layer thermal conductivities as well as increase in thermal boundary conductance for thermal interface materials is currently being studied [125, 126].

Being able to manipulate thermal conductivity with external fields would also be a critical element of the rational design paradigm. The weak interaction of electrons and phonons implies that use of electric fields to manipulate thermal conductivity has been limited to structures where electronic contribution to heat transport is significant [127]. Other approaches could involve the use of materials with domain walls that respond to external magnetic fields [128] or even phase change materials that respond to external thermal fields [129].

The understanding of the role of a periodic arrangement of surfaces on phonon transport is also beginning to emerge [34, 92]. Periodic structures are currently being used to probe the wave nature of phonons and tune the thermal transport of materials. The interaction of phonons with smooth surfaces in semiconductor nanowires (e.g. superlattice or core–shell nanowires) at low temperatures also provides new opportunities to explore the phonon wave domain in nanowires.

Another open question in nanoscale thermal transport has been the ability of phonons to propagate and contribute to thermal transport in non-crystalline materials (e.g. polymers, amorphous silicon [121, 122]). Amorphous nanowires can also be ideal structures to fully understand the transport of phonons in both crystalline and non-crystalline materials and answer open questions related to the movement of thermal vibrations in randomly arranged atomic distributions.

In summary, this review has shown that the development of new fabrication and measurement techniques combined with advances in theory and predictions of thermal phonon transport has been central to advancing control of nanoscale thermal conduction. These advances have also been critical for a fundamental understanding of transport of phonons and heat conduction in semiconductor nanowires. Such recent progress on understanding and controlling thermal transport has arisen by manipulation of central physical properties of phonons; yet there are significant questions that need to be answered to propel scientific and technological progress. From this unprecedented ability to understand, design, and grow nanowires with precise thermal properties and phonon characteristics we can expect a new era of thermal material designs and developments.

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