

Lattice thermal conductivity of SiC nanowires

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Abstract

We present non-equilibrium classical molecular dynamics simulations for the lattice thermal transport of SiC nanowires and bulk β -SiC. The thermal conductivity of the nanowires is strongly reduced compared to the SiC bulk value. In our approach only the phonon contribution to the heat flow is considered, neglecting any electronic components. We investigate the dependence of the thermal conductivity on the wire cross section and consider the influence of different wire surfaces on the thermal transport.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Modern electronics devices have sizes below 100 nm and heat dissipation is a major issue. Generally, thermal transport is mainly diffusive but for nanodevices, when the phonon mean free path is larger than the device dimensions, ballistic contributions might become important. Early predictions that superlattices and nanowires would have improved performance as thermoelectrics [1] attracted much attention and many studies were devoted to the thermal properties of superlattices [2, 3], nanowires [4–9], and superlattice nanowires [10–12], in an effort to find new, better, thermoelectric materials [13–16]. Recently a systematic study of semiconductor nanowires pointed out that the thermal conductivities in the nanoscale cannot be extracted from the bulk thermal conductivities of the materials [17]. Understanding thermal transport in the nanoscale and designing materials with very high or very low thermal conductivities would have an impact on electronic, as well as optoelectronic devices, and will also help the design of thermal barriers or new thermoelectric materials.

Concerning the thermal properties in the nanoscale, Si nanowires are one of the most studied systems [7–10]. Recent measurements of thermal conductivity [6, 12] renewed interest in theoretical modeling and many studies used either the Boltzmann equation or molecular dynamics simulations to explain the experimental results [7–10]. In dielectrics, (e.g. semiconductors) the thermal flow is mainly attributed to phonon transport, while in semiconductor nanowires the modification of the phonon velocities due to confinement [10] as well as surface and interface scattering increase the thermal resistance.

Silicon carbide is an interesting material with potential applications in high power electronics due to its high breakdown field, and high thermal conductivity, while the combination of mechanical and chemical stability make it a possible candidate for use in high temperatures, high power, high frequency, and in harsh environments. Nanowires and other nanostructures of SiC have been fabricated using several methods such as chemical vapor deposition, arc-discharge, or using carbon nanotubes in vapor–solid, or solid–solid reactions [18, 19]. Very thin nanowires were also reported with only a few nanometers' diameter [20]. In some cases the fabricated SiC nanowires had a crystalline core coated with amorphous material [21].

Theoretically, the methods to calculate the thermal conductivity in the nanoscale generally fall in two main categories: methods that solve the Boltzmann equation and molecular dynamics simulations. The Boltzmann equation approach was used in various levels of sophistication to calculate the thermal conductivity [22, 23]. The simpler approach for nanowires is to use the Kallaway formula [24], considering the interface scattering. Going one step further and modifying the Kallaway–Hall approach by using the bulk phonon dispersion gives results that can explain the experimental findings for nanowires with diameters larger than 30 nm [9, 25]. Improvements in this approach have taken into account the nanowire phonon dispersion which is modified due to confinement. The studies on Si and Ge nanowires also reported good agreement with the experimental results [26, 5]. A direct solution of the Boltzmann equation is also possible either analytically or numerically, using the correct boundary conditions for the nanostructures [7, 26].

Overall the Boltzmann equation approach has some advantages since many effects can be included and systematically studied, while good agreement with experiment was obtained in many cases. The method is also computationally efficient compared with the atomistic, molecular dynamics, methods. However, in many cases the predictive power is limited since adjustable parameters are required to allow comparison with experiments.

In recent years, molecular dynamics methods have also been used to study thermal transport. There are mainly two approaches: the equilibrium method which is based on the Green–Kubo formalism and linear response that connects the thermal conductivity to the correlation of the heat current (see e.g. [27] and references therein). The second so-called non-equilibrium or *direct* approach calculates the thermal conductivity using the Fourier law after a temperature gradient is established in the sample by creating a steady heat flow. The two approaches were shown to produce the same results in bulk Si if convergence is reached [27]. Finite size effects have a different influence on the two methods and require special attention [28]. The molecular dynamics method is useful for very thin layers, nanowires, and structures with dimensions of a few nanometers.

Essentially, the molecular dynamics approach requires no assumptions on the nature of the scattering mechanisms that dominate the thermal transport. On the other hand, the method is computationally very intensive and depends critically on the choice of the interatomic potential used. The computational requirements restricted all studies up to now to classical empirical potentials, since more realistic tight-binding methods are computationally more demanding. This is the main drawback of the method since the quality of the interatomic potential can influence the results [29]. The molecular dynamics method was also compared with the Boltzmann equation approach [30] and satisfactory agreement was found.

Lately, there is an increased interest in the thermal properties of the nanoworld [13, 16]. Atomistic simulations can give detailed information about the influence of interfaces which is not easily accessible by other methods, and they are also useful in nanosystems where the atomic structure cannot be ignored. We will use the ‘direct’ molecular dynamics method to study SiC nanowires with transverse dimensions from 2 to 4 nm; our study is more relevant to the thinnest nanowires fabricated [20].

2. Theoretical method

A classical molecular dynamics (MD) simulation computer code was developed using standard methods [31]. The equations of motion are integrated using a velocity-Verlet algorithm. The interaction between the atoms is described with an empirical, classical potential which depends only on the relative position and the type of atoms. Short range potentials allow the study of systems with a few thousand atoms.

For SiC there exist several polytypes, one of the most common is the zinc-blende structure (β -SiC). There are also a few empirical potentials developed for SiC

and some comparative studies in order to evaluate the potentials [29]. We used the potential developed by Tersoff for SiC. The form of this potential was used for Si and C and was also extended to binary systems like SiGe and SiC. This potential was used by Halicioglu [32] to study the energy and structure of the β -SiC (100) surface. We have repeated and confirmed those calculations to test our method. Additionally a version of the potential with a varied cutoff was used to calculate full phonon dispersions, surface relaxations, and thermal expansion coefficients [33]. More recently Shimojo *et al* have successfully used a new potential to describe the structural transformation of SiC under pressure [34]. The Tersoff potential with small modification was used to study the thermal conductivity of bulk SiC and the influence of native defects using the equilibrium MD method [35]. In that study reasonable agreement with experiment was found when a temperature rescaling was used to account for quantum corrections at low temperatures. A comparison of different empirical potentials for SiC was recently reported by Crocombette *et al* [29] in simulations of the thermal conductivity of irradiated SiC. All the potentials are designed to reproduce mainly bulk properties and we have chosen the Tersoff potential parameterization for SiC [36]. Despite the fact that this potential underestimates the thermal conductivity of bulk β -SiC, as demonstrated by Crocombette *et al*, eventually the differences between parameterizations are negligible if we consider SiC with a different nanostructure [29], as we do in this work.

The nanowires and the bulk were prepared at the zero temperature equilibrium lattice constant $a = 0.4321$ nm and then allowed to reach equilibrium at the desired temperature for 50 000 time steps using a Berendsen constant temperature thermostat [31]. For the bulk we used long rectangular supercells with a square cross section $2a \times 2a$ which extended a few hundred nanometers along the [100] direction. A periodic boundary was used in all three dimensions. The SiC nanowires were constructed in a similar manner, but finally removing some outer layers to achieve either Si or C terminated wires with a square cross section. We consider wires with three different cross sections $5a \times 5a$ which gives approximately 2.05 nm \times 2.05 nm, uniformly terminated wire, 2.92 nm \times 2.92 nm ($7a \times 7a$), and 4.21 nm \times 4.21 nm, a $10a \times 10a$ wire. We use periodic boundary conditions in the wire direction with a varying period of $L \approx 20, 30, 40$ nm in order to check any influence of finite size effects on our results. Since the transverse dimensions of the nanowires are much smaller than the phonon mean free path, no finite size effects were observed, as is discussed below, but the results obtained for the wires of different periodicity were used as an error estimate for our calculations. The size of the systems studied ranged from around 8000 to almost 70 000 atoms.

Thermal expansion is small in SiC [35] and was neglected in this study, moreover using a free boundary for the wires helps to partially release the stress build. The initial equilibration was followed by the non-equilibrium MD calculation [27] where a temperature gradient is established by adding and subtracting heat at different parts of the nanowires. The time step was chosen $\Delta t = 0.3$ fs to insure adequate

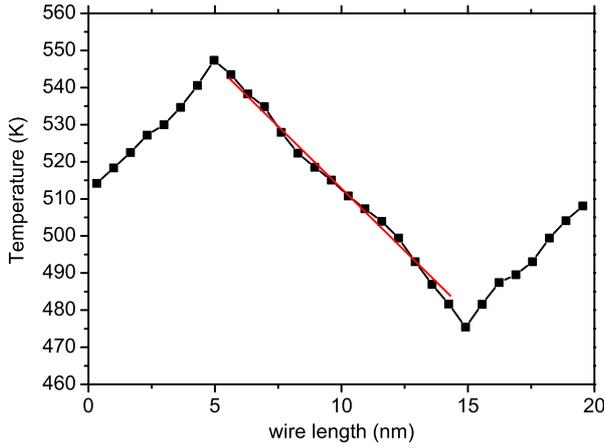


Figure 1. Variation of the local temperature along the wire for a nanowire of $(2.92 \times 2.92 \text{ nm}^2)$ cross section. The straight line is a least squares fit to the data between source and sink.

convergence. Heat was added at $L/4$ and subtracted at $3L/4$ on each time step and the thermal conductivity is calculated from the local temperature variation. The procedure suggested by Jund *et al* [37] was used in order to achieve energy conservation during the MD run. The heat current is given by [27] $J = \Delta\epsilon/2A\Delta t$, A is the wire cross section, we have tried different $\Delta\epsilon$, typically $\Delta\epsilon = 1.7 \times 10^{-4}$ eV for bulk and $\Delta\epsilon = 4.3 \times 10^{-4}$ eV for nanowires was used.

The results for a typical example of such a run are shown in figure 1, where we show the temperature gradient for the case of a wire of square cross section and edge of 2.92 nm and a supercell length 20 nm. We consider slices of the wire where the local temperature was calculated by averaging the kinetic energies of the atoms inside each slice, typically 30 slices are used. The gradients were obtained using the points in the linear regions, excluding the points for slices of the source and sink as well as the points at the immediate vicinity. We apply periodic boundary conditions along the wire direction so that two temperature gradients can be extracted. The difference in the two slopes is usually small and gives an estimate of the error, in practice we calculate the average of the two slopes. The thermal conductivity κ is obtained directly from the Fourier law:

$$J = -\kappa \nabla T \quad (1)$$

where J is the heat current and ∇T the temperature gradient. In the case of nanowires, the local temperature in each slice of the wire reaches convergence after $\sim 4\text{--}5 \times 10^5$ time steps. For the bulk calculations 4–5 times more time steps are required. The averaging for the calculation of the thermal conductivity included only the last 5×10^5 MD steps. The initial time during which a heat imbalance was applied was enough to establish a steady heat current in all cases presented here. Free boundaries are used in the calculations on the nanowires and this was problematic in some cases, especially for C terminated wires at higher temperatures. Moreover in some cases the initial equilibration was not sufficient and imposing the heat source and sink resulted in a small increase (5–10 K) in the wire equilibrium temperature.

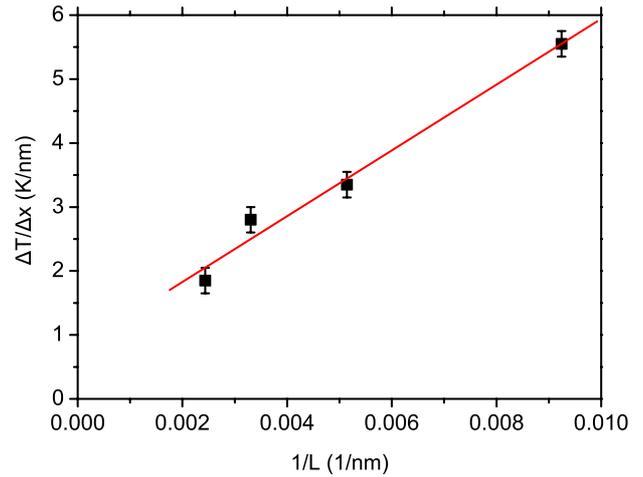


Figure 2. Dependence of $\Delta T/\Delta x$ on the inverse of the supercell length $1/L$ for bulk β -SiC at $T = 500$ K. Extrapolation to $1/L = 0$ gives a value $\Delta T/\Delta x = 0.80 \pm 0.21$ which corresponds to $\kappa = 77 \pm 20 \text{ W m}^{-1} \text{ K}^{-1}$ in the limit of infinite supercell length.

3. Results and discussion

3.1. Bulk β -SiC

The measured thermal conductivity of bulk SiC is $\kappa \sim 330 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature and drops to $\kappa \sim 210 \text{ W m}^{-1} \text{ K}^{-1}$ around 500 K (look at Li *et al* [35] and references therein). The non-equilibrium MD is probably not the method of choice to study bulk properties, since the thermal conductivity is rather high, the mean free path of phonons is long, and big supercells are required to achieve converged results. However, in order to have a reference for the calculations of nanowires we first consider bulk β -SiC. We use long supercells with $0.8642 \times 0.8642 \text{ nm}^2$ cross section and length ranging from 100 to 400 nm. Following the arguments of Schelling *et al* [27], we consider the dependence of $\Delta T/\Delta x = -J/\kappa$ on the inverse of the supercell length which is shown in figure 2. The linear dependence allows the extrapolation to supercells of infinite size and we extract a value $\kappa_{\text{theo.}} \sim 77 \pm 20 \text{ W m}^{-1} \text{ K}^{-1}$ which is less than half the experimental value. However, our bulk value is in accordance with other equilibrium MD calculations of the thermal conductivity of β -SiC using the same potential [29].

3.2. SiC nanowires

For nanowires it is interesting to investigate the influence of the wire cross section on the thermal conductivity. Additionally we study the effect of different surface terminations by considering wires of the same cross section but different surfaces with Si only and C only.

The variation of the thermal conductivity with the wire transverse dimension is shown in figure 3 for both Si and C terminations at a temperature of 500 K. The thermal conductivity is strongly reduced compared to the bulk value, due to the confinement which reduces the phonon mean free path as well as to the phonon scattering on the wire surface. This is the general trend reported for different semiconductor

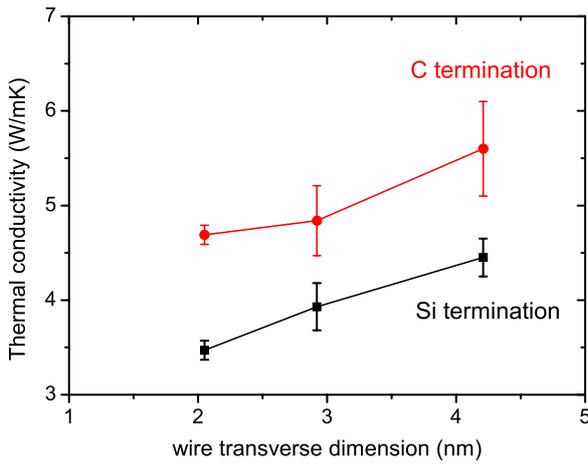


Figure 3. Thermal conductivity of SiC nanowires with C (circles) and Si (squares) terminations at $T = 500$ K for wires with square cross sections and different transverse dimensions.

nanowires. Our results show that the C terminated wires have almost 20% higher conductivity compared to the Si coated ones. An important feature is the increase of the thermal conductivity with the wire's transverse dimension. Previous studies on Si nanowires of similar dimensions [4] reported a power law increase of κ with the wire's transverse dimensions, but our calculations are not sufficient to resolve whether the increase is linear or power law. Interestingly this increase of κ seems to be similar for both terminations.

The difference between Si and C terminations is interesting and deserves further study. In figure 4 we show representative snapshots of Si and C terminated wires of the same cross section, both snapshots are taken towards the end of the simulations with a steady heat current present. An interesting observation is that the Si surfaces appear to have stronger disorder compared to the C ones and this is a general trend observed in wires with different cross sections. This observation supports the lower thermal conductivity values for the Si terminated wires due to stronger scattering on a more disordered surface. We can compare our results with the work of Khitun *et al* [26]. In that work, the phonon

dispersion for a free and a clamped surface nanowire of 20 nm diameter was calculated. The difference in group velocity between the different terminations was found to be small so there was little change in the thermal conductivity. However, a clamped surface boundary generally gave lower thermal conductivity. The influence of free and rigid boundary conditions was discussed also by Volz and Chen [4] but their results did not show any clear trend. However, those authors report that the thermal conductivity decreases as the scattering at the wire surface becomes more diffusive. This was also the conclusion of Zoo and Balandin [5]. Our results also support this conclusion.

On the other hand the effect of surface scattering is probably more complicated, as was demonstrated by Mingo and Yang [38] who considered thermal transport in nanowires coated with an amorphous material and found that the phonon relaxation length has a minimum for a certain strength of the coupling between the wire and the coating and increases for both stronger and weaker coupling. This means that the strength of the coupling to the surface atoms is an important parameter which is usually neglected in the solution of the Boltzmann equation. In a Boltzmann equation approach, different terminations are usually modeled by different interface specularity parameters. From the calculations of Volz and Chen [4] we can see that the increase of thermal conductivity with the wire diameter does not depend on the specularity parameter. This is consistent with our MD results shown in figure 3 where the dependence on the cross section is similar for both terminations.

To conclude this part, our study goes beyond a model parameter study and gives some quantitative information on the influence of termination of SiC nanowires by using realistic interatomic potentials. To our knowledge, so far there has been no measurement of the thermal conductivity of SiC nanowires. However, the structure of the SiC nanowires strongly depends on the fabrication method. This lack of experimental data on well characterized samples motivated our generic model with a square cross section in the [100] direction because the geometrical structure is simple and remains the same for all the wires and different terminations considered. The advantage of simple square cross section is that the effects of bond strength

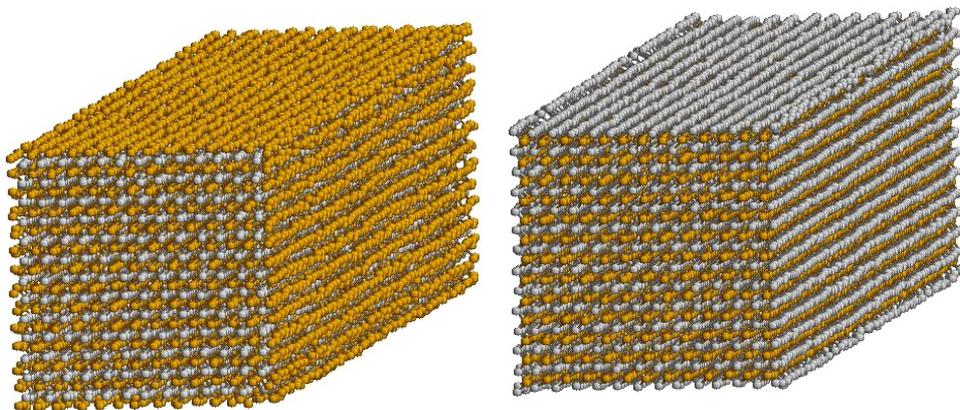


Figure 4. Ball and stick model of the SiC nanowires considered in this work. The figures are snapshots of MD runs at the same temperature for 2.92×2.92 nm² with Si termination (left) and C termination (right) both simulations are for $T = 500$ K.

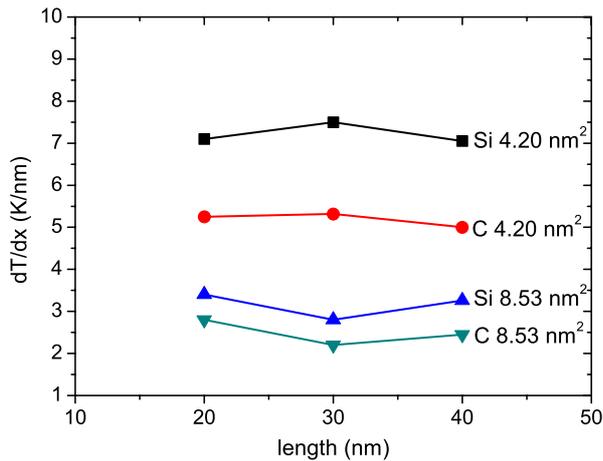


Figure 5. Dependence of the temperature gradient of SiC nanowires with different cross sections ($2.05 \times 2.05 = 4.20$ and $2.92 \times 2.92 = 8.53 \text{ nm}^2$) on the size of the supercell along the wire direction at $T = 500 \text{ K}$.

and different mass of the atoms on the surface can be studied without any additional complicating factors such as the surface geometry. Our prediction is that C terminated wires will show higher thermal conductivity compared to Si terminated ones of the same dimensions and shape.

Previous MD studies of the thermal conductivity in bulk Si report convergence problems and finite size effects, if supercells smaller than the phonon mean free path are used [27]. For nanowires, the mean free path is mainly controlled by the wire cross section and we expect only a small influence on the nanowire length. This is confirmed by our calculations, as is seen in figure 5 where we show the calculated temperature gradient (dT/dx) as a function of the length of the supercell along the wire direction for different wires considered in this study. It is clear that the results are well converged and, contrary to the case of bulk considered above, finite size effects are less crucial for the nanowires.

Surface scattering is generally temperature independent in bulk systems [39]. We have chosen the wire with the smaller cross section $2.05 \text{ nm} \times 2.05 \text{ nm}$ and studied both C and Si terminations. The temperature dependence of the thermal conductivity is shown in figure 6. Our results show a very small variation of κ for temperatures 400–600 K. The only exception is C terminated wires at 600 K where the calculations show a clear drop. For higher temperatures and C terminated wires it became very difficult to obtain a constant temperature equilibrium, since we observed diffusion and atomic rearrangement of the nanowire surface. This temperature induced disorder for C terminated wires at $T = 600 \text{ K}$ and above, produced by the Tersoff potential for SiC, is the reason for the drop of the thermal conductivity for C termination shown in figure 6.

The calculated results depend on the accuracy of the interatomic potential. Recently Broido *et al* compared the calculated thermal conductivity of Si using the most popular classical potential parameterizations of Stillinger–Weber and Tersoff [40]. Both potentials gave satisfactory agreement with experiment for bulk at low temperatures. However, for higher

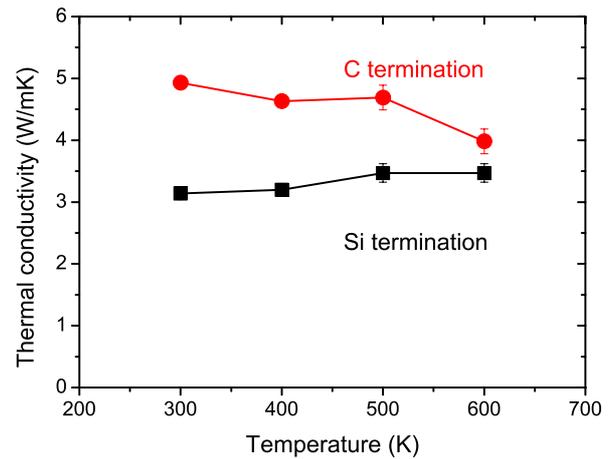


Figure 6. Temperature dependence of SiC nanowires of $2.05 \times 2.05 \text{ nm}^2$ for Si (squares) and C (circles) terminations.

temperatures the calculated conductivities were 2–4 times larger than the experimental values. This study revealed that the classical potential parameterizations are fitted to reproduce the elastic constants and this is not enough for modeling thermal conductivity at higher temperatures where group velocities away from the zone center are important. Despite this fact, both parameterizations gave similar qualitative behavior. Generally, for moderate temperatures, heat is carried by the phonons at the zone center. Since the potential was fitted to the elastic constants of SiC good agreement with experiment should be expected for low temperatures. However, comparison with experiment should be used with caution since for lower temperatures quantum effects which are beyond the scope of this work become important. Despite the above problems, due to the inaccuracies of the classical potentials used, for nanostructures the differences between parameterizations seem to be less crucial, as was demonstrated recently [29].

4. Conclusion

We report calculations for the thermal conductivity of bulk β -SiC and SiC nanowires with cross sections ~ 4 – 17 nm^2 . The thermal conductivity is strongly reduced in the nanowires compared to the bulk and generally it will depend on the presence of defects on the surface. Here we have studied a simple case of a uniform termination and showed that κ changes by 20% for different surfaces, and increases with increasing cross section.

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