Thermal conductivity and Kapitza resistance of diameter modulated SiC nanowires, a molecular dynamics study

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Abstract. The thermal conductivity of diameter modulated SiC nanowires is computed with the non-equilibrium Molecular Dynamics (NEMD) method. The two main polytypes 3C (zinc-blend) and 2H (wurtzite) of SiC nanowires are investigated, but also the superlattice SiC nanowires with shape modulation. For the case of the shape modulated nanowires the Kapitza resistance is calculated with both NEMD and Equilibrium MD (EMD) methods. This thermal resistance is related with the restrictions between two different cross sections. Finally, we proceed to the physical explanation of this phenomenon with the help of the partial densities of states of phonons.

1. Introduction
Nanostructures and nanostructured materials are interesting candidates for a wide range of applications. Molecular-Electronics, quantum computers, actuators, sensors and molecular machine are some of the applications of the modern nanotechnology [1]. Their novel functions involve unique mechanical, thermal and electronic properties. A crucial question is whether they contact efficiently or not the heat current and whether they remain stable mechanically at a given operational temperature. Silicon Carbide (SiC) is an important semiconductor with wide-band-gap electronic structure that attracted early interest because of its high mechanical strength, due to the sp2 and sp3 bonds between silicon and carbide atoms, high chemical stability and high thermal conductivity. It is used broadly in nanoelectronics, while, as it is one of the hardest materials, it is suitable for devices under extreme environments. Novel hydrogen storage devices and a series of applications in catalysis, biomedical and optics are some of the uses for this material [2]. SiC sustains a variety of stable nanostructures, like nanowires, nanotubes or nanocages, nanobelts, nanorods etc [3, 4, 5, 6]. Furthermore, SiC has a large number of lattice structure and stacking faults polytypes, making the material an interesting candidate for a great number of applications [4]. The thermal transport in nanoscale is mainly ballistic as the phonon mean free path is of the same order of magnitude as the characteristic dimensions of the nanostructures, thus the classical Fourier’s law of thermal conduction is not valid anymore. At these scales the measurement of the thermal
conductivity is a difficult task and simulations are necessary tools for the prediction of the thermal conductivity and the theoretical investigation of the underneath physical phenomena related to the heat transport at the nanoscale [7, 8]. Molecular Dynamics simulations methods are proved for their quality to predict correctly the thermal properties of semiconductors or insulators where the phonons are the main heat carriers and for temperatures higher of the Debye temperature. Among the MD simulation approaches to calculate the thermal conductivity, there are two main methods: the non-equilibrium (NEMD) based on forcing a temperature gradient on the system and the Equilibrium (EMD) within the Green-Kubo approach. We have to mention at this point that the EMD method is adequate and very efficient for homogeneous, isotropic systems, but one should use it very carefully in the case of nanostructures, where the surface and interfaces ratio to volume is getting extremely high.

The outline of the present paper is as follows: in section 2, the thermal conductivity of the two main polytypes of SiC nanowires function of its cross sections and lengths are presented. Furthermore we consider diameter modulated SiC nanowires and compare the values of the thermal conductivity of these nanowires with the pure ones. In section 3 we introduced the restriction resistance due to the necks for the diameter modulated nanowires, giving results obtained by EMD and NEMD methods, while in section 4 we investigate the partial density of states around these restrictions to explain the decreased thermal conductivity of these modulated nanowires compared to the constant diameter nanowires.

2. Thermal conductivity of pure and modulated SiC nanowires

The two main polytypes of SiC are studied in this section, the hexagonal (2H) and the cubic (3C). Even if the purpose of the article is the shape modulated 2H nanowires, with this first section, we validate our method and we communicate the results for the two polytypes, adding to the existing literature results for nanowires with large cross-sections and lengths. These polytypes are characterised by the stacking sequence of the biatom layers of the SiC structure in the c-direction, which is the –AB- for the 2H and the –ABC- for the 3C polytype. In this section the thermal conductivity is calculated by using only the NEMD method. The NEMD method is similar to the hot plate experimental set-up and in this method a temperature difference is imposed to the edges of the structure. Knowing the heat flux and the temperature gradient we can calculate the thermal conductivity via the Fourier law [9, 10, 11, 12]. We use the code LAMMPS [13] and the Tersoff potential [14] for the description of the interatomic forces. Free boundary conditions are used in x and y directions, while in the z direction the use of fixed atoms belonging at the two bilayers at the edges of the nanowire assure the stability of the nanowire. The mean temperature is set to 300K, while a temperature difference of 30K is imposed to the two thermostats situated at the two edges after the fixed atoms. At the subsection 2.1 the thermal conductivity of the two pure polytypes is presented function their cross-section and their lengths. In the 2.2 subsection the results of the thermal conductivity of diameter modulated 2H SiC superlattice nanowires are given. These kind of modulated nanowires are promising candidates for high thermoelectric energy conversion [15, 16].

2.1. Thermal Conductivity of pure SiC nanowires

The thermal conductivity of the 2H and the 3C polytypes of SiC nanowires is calculated as a function of their lengths and the cross sections (figure 1 and 2). The thermal conductivity of the 2H polytype is higher than the one of the 3C polytype for both studies (cross-section and length dependences). We also note that the thermal conductivity is increased when increasing both the length of the nanowire and the cross-section and reach a plateau related to the phonon mean free path. This trend was expected as it has been observed for other regular nanowires as for example silicon nanowires [17]. Papanikolaou studied also the thermal conductivity of only cubic SiC nanowires and our values are in a good agreement with his results (3.5 to 4.5 W/mK for nanowires with Si or C atoms termination) [18]. For the study of the length effect, the cross-section of the nanowires is kept constant equal to 15.7nm², while for the study of the cross-section the length kept constant and equal to 25.5 nm.
2.2. Thermal Conductivity of diameter modulated SiC

With the development of new growth techniques and varying the temperature and the pressure, one can obtain nanoengineered modulated nanowires. The possible modulations are diameter, lattice structure or lattice orientation, doping concentration and composition [15, 16, 18, 19, 20, 21]. This kind of modulated nanowires can combine potentially the properties and functions of superlattices and nanowires.

A diameter modulated nanowire is depicted in figure 3. We consider here only the 2H polytype. The results for the thermal conductivity of the diameter modulated nanowires as a function of the nanowire’s length are presented in figure 4. The small section for the pure nanowires is set to 15.67nm², while the large section to 35.25nm². For the diameter modulated nanowires there is an alternation of these two cross-sections, with a periodicity of the superlattices chosen to be 12 bilayers. At this kind of modulation the underneath physics becomes more complex and more interesting as we will show at the next sections. For comparison the thermal conductivity of the pure 2H polytype for the two cross sections equals to the sections chosen for the diameter modulation of SiC nanowires are presented.

The nanowire’s diameter modulation induces heat flux line constriction that increases the thermal resistance of the nanowire compared to a nanowire with a diameter equal to the larger diameter of the modulations. On the contrary, by intuition, the thermal resistance of the modulated nanowire should be
smaller than the one of the nanowire with a constant diameter equal to the smaller diameter of the modulations. Thus, on the figure 4, the thermal conductivity of the modulated nanowire should be smaller than the thermal conductivity of the nanowire with a section of 35.25 nm² but higher than the thermal conductivity of the nanowire with a section of 15.67 nm². Actually, the thermal conductivity of the modulated nanowire is smaller than the thermal conductivity of the smaller nanowire contrary to the first intuition. Thus another physical phenomena, linked with phonon transmission - from one section to the other one- might be invoked. This reduction of the thermal conductivity can be attributed in the reduction of the group velocity and the interaction of the phonon mean free path, which is around 20 nm in our case with the characteristic sizes of the studied nanowires. The thermal resistance and the density of states (DOS) are studied at the next two sections to understand deeper the physical phenomena related to the modulation.

3. Thermal restriction resistance

With NEMD and the Equilibrium Molecular Dynamics (EMD) method, we studied the influence of the Kapitza resistance. We consider in all calculations that follow, the same diameter modulation of the 2H SiC nanowire as in the previous section, with smaller this time cross-sections for the shake of computational time. We name this Kapitza resistance between the two different cross-sections as thermal restriction resistance. The reason for this is the need to differentiate the Kapitza resistance which is defined as the thermal boundary resistance between two different materials of the same or different phases, from this virtual interface between the same material.

In the EMD method the thermal resistance $R_{TR}$ between two systems with temperature difference $\Delta T$ could be calculated by the following equation [22]:

$$ R_{TR} = k_B \int_0^\infty \frac{\langle \Delta T(O) \Delta T(t) \rangle}{\langle \Delta T(O)^2 \rangle} dt \left( \frac{1}{N_1} + \frac{1}{N_2} \right) $$

(1)

Where, $N_1$ and $N_2$ refer to the number of degrees of freedom of the two parts in thermal contact, respectively. By calculating the autocorrelation function (ACF) of the temperature difference fluctuations at equilibrium (cross correlation of the temperature difference with itself), the thermal resistance could be obtained. The temperatures could be acquired in EMD from kinetic energies. The final ACFs were derived from the average of 20 trajectories with different initial velocities. The restriction resistance for diameter modulated nanowires is calculated with EMD method and it is equal to $1.74 \times 10^{-10}$ m²K/W.
The NEMD method is based on the calculation of temperature difference at the two sides of the interfaces and the knowledge of the heat flux \( (R=\frac{DT}{q}) \). With the NEMD method the average internal thermal resistance for 2H SiC nanowires is equal to \( 6 \times 10^{-11} \text{ m}^2\text{K}/\text{W} \). The diameter modulated nanowires show a restriction resistance of \( 0.9 \times 10^{-10} \text{ m}^2\text{K}/\text{W} \) almost double than the internal one. The restriction resistance is increased in increasing the temperature. The variation of the cross-sections also plays a role in the constriction resistance; we studied two kinds of diameter variations from \( 8.81\text{nm}^2 \) to \( 15.67\text{nm}^2 \) and from \( 8.81\text{nm}^2 \) to \( 47.98\text{nm}^2 \). In the first case the restriction resistance was \( 0.8 \times 10^{-10} \text{ m}^2\text{K}/\text{W} \) and in the second \( 1.2 \times 10^{-10} \text{ m}^2\text{K}/\text{W} \). In contrary, it seems that the periodicity of the superlattices does not influence the constriction resistance.

The two methods even if they do not give the same results, they provide the same tendencies. The restriction resistance is double than the internal resistance of the nanowire. Finally we observe that this resistance is localised in very few monolayers around the nanowire restrictions.

4. Density of States

The density of states for the case of diameter modulated 2H nanowire is studied with cross-sections varying from \( 8.81 \) to \( 15.67\text{nm}^2 \), the same slab like in section 3. The phonon density of states of the particle is numerically obtained by decomposing the time correlation function of the atomic velocities into the Fourier space as \[23, 24\]:

\[
P(\omega) \propto \int_0^\infty \sum_i \langle v_i(0) \cdot v_i(t) \rangle e^{-i\omega t} dt
\]

Where \( \omega \) denoted to the angular frequency. Velocities of the atoms are calculated from the integration of the second Newton’s law.

In figure 5 the partial density of states is calculated for the small and large cross-sections far from the interface and for the first adjacent layers for the both sides of the interface. The interest is focused in three areas: a. for intermediate frequencies 25 to 30 THz where there is a decrease of the density of states of the adjacent layers in comparison to the constant section nanowires, b. for small frequencies 0 to 10 THz (see figure 6 for more details) where confinement modes are appeared at the first layer of
the big cross section and c. for big frequencies 30 to 37 THz where the additional local maxima of the density is attributed to the interfacial and surface phonon modes (see figure 7 for more details). In figure 8, there is a picture showing the bilayers considered for these calculations. The DOS at the first layer of the big cross section exhibits additional low-frequency peaks (see figure 6 for more details). These low-frequency peaks are only shown at the cross section layers, indicating phonon confinement. Similar phenomena are also observed in other works [25, 26, 27]. The phonon interactions might be altered due to this confinement, and as a result a higher Kapitza resistance was found for diameter modulated nanowires.

![Figure 6. Density of states for 4 distinguished groups for frequencies 0 to 10 THz.](image)

![Figure 7. Density of states for 4 distinguished groups for frequencies 28 to 40 THz.](image)

![Figure 8. The groups considered for the calculation of the partial density of states. 1. group of atoms far from the interface for the small cross section nanowire (8.81nm²) and 2. group of atoms for the first bilayer closest to the interface. 3. and 4. groups of atoms for the large (15.57nm²) cross section nanowire far and the first bilayer closest to the interface.](image)

5. Conclusions

We have predicted the thermal conductivity of the two main polytypes of SiC nanowires, the 3C and the 2H. It is the first reported calculation for the two types with such dimensions completing the existing litterature. The thermal conductivity of the 2H polytype is higher than this of the 3C. The length and the cross section influences the thermal conductivity for both cases in the same way: increasing of the length results in increasing of the thermal conductivity till the length is getting bigger than the phonon mean free path of the phonons which is around 20nm, and also increasing the cross section results in increasing the thermal conductivity.
The study of the diameter modulated nanowires show that their thermal conductivity is even less than the thermal conductivity of the smallest cross section nanowires with constant diameter. This decrease is related with an additional thermal resistance occurred at the restrictions (passing from the large cross sections to smaller ones and vice-versa). We define this thermal resistance as restriction resistance and we show that it is double than the internal thermal resistance. The density of states study showed that the phonon modification is related to the confinement of the modes and the additional surface modes appeared with the diameter modulation. We believe that a certain number of phonons are trapped in the large cross sections and this might be a way to decrease further the thermal conductivity of nanowires, when this is the aim, e.g. thermoelectric materials. Further study of the parameters of the diameter modulation is needed and the lattice structure modulation is in our future plans. In this point we have to mention that it will be interesting to study the transmission coefficient of phonons at these restrictions. We believe that the transmission coefficient will give more clear picture of the phenomenon and more quantitative results.

6. References

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