

Atomistic Simulations of Heat Transport in Silicon Nanowires

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We present a series of molecular dynamics, lattice dynamics, and Boltzmann transport equation calculations aimed at understanding heat transport in Silicon nanowires. In agreement with recent experiments, we find that the computed thermal conductivity strongly depends on the surface structure. It may be as high as that of bulk Si for crystalline wires, while wires with amorphous surfaces have the smallest thermal conductivity, about 100 times lower than the bulk. Two, combined effects are responsible for this dramatic difference: the presence, at disordered surfaces, of extended, nonpropagating modes analogous to heat carriers in amorphous Si, together with decreased lifetimes of propagating modes.

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As the basic constituent of semiconductor electronics, Silicon is one of the best known materials, cheap, and readily available. It would therefore be highly desirable to broaden its utilization to renewable energy applications. Recently, it was proposed that Silicon, engineered at the nanoscale, may become an efficient thermoelectric material [1,2], unlike its bulk form [3]. Even though Silicon nanostructures have been regarded as potential building blocks of thermoelectric materials for several years [4], only recently it has been possible to synthesize nanowires (SiNW) with controlled size, growth direction, and surface properties [5], so as to build homogeneous wafer-scale arrays with high thermoelectric efficiency. Such efficiency is defined in terms of the figure of merit $ZT = \frac{\sigma S^2}{\kappa_I + \kappa_e} T$, where σ is the electronic conductivity, S the Seebeck coefficient, κ_I and κ_e are the ionic and electronic thermal conductivity, respectively, and $\kappa = \kappa_I + \kappa_e$. In recent experiments [1,2] using SiNWs, $ZT \approx 1$ has been achieved, which is about a 100-fold improvement over the value obtained for bulk silicon. Boukai *et al.* [2] have identified electron-phonon interaction as one of the main effects responsible for an enhancement of the Seebeck coefficient of wires, and thus for increased ZT . According to Hochbaum *et al.* [1], it is instead the low ionic thermal conductivity of wires that is mainly responsible for high ZT values. This interpretation is consistent with the conclusions of electronic structure calculations [6] of thin SiNW (diameter $d \approx 1\text{--}3$ nm), that showed that one may achieve $ZT \approx 1$ only if κ is reduced by at least 2 orders of magnitude with respect to bulk values. Model calculations of heat transport [7–9] in SiNWs have reproduced some of the trends observed experimentally for κ as a function of size down to $d \approx 25\text{--}30$ nm. However, it is yet unknown whether size reduction is the main factor determining the measured value of κ , and if further decreasing the diameter of wires below 10 nm may yield higher ZT . For smaller d , atomistic simulations [10,11] have so far given contradicting results about the specific values of κ that may be attained.

In order to gain a microscopic understanding of heat transport in SiNWs, we have performed a series of mo-

lecular dynamics (MD) simulations for wires with $d \approx 1\text{--}4$ nm [12]. We have used an equilibrium MD approach [13], already successfully applied to study heat transport in bulk systems [14–16] and nanostructures [17,18], in which κ is computed by a Green-Kubo method [19], and the empirical force field by Tersoff is employed [20]. We have then carried out detailed analysis of heat carrying vibrations based on the Boltzmann Transport Equation (BTE), and on a nonperturbative approach based on linear response originally proposed for amorphous Silicon (*a*-Si) by Allen and Feldman [21] (hereafter referred to as AF approach). Only κ_I is considered, as the electronic contribution, previously obtained by electronic structure calculations, remains smaller than 0.1 (W/m)/K for concentrations of dopants up to 10^{18} cm^{-3} [6].

To probe the effects of surface morphology, we considered three types of SiNW, grown along the (001) direction: (i) ideally, *H*-terminated crystalline wires with round cross section; (ii) crystalline wires with square cross section and (2×1) -like reconstructed, *H*-terminated surfaces; and (iii) wires with a crystalline core and amorphous surface layers of varying thickness [1,22]. The latter models were generated by heating crystalline wires to 2400 K (the melting temperature of the Tersoff model is ~ 2500 K) for 40 to 160 ps. The thickness of the amorphous shell formed is proportional to the annealing time. The SiNWs were then quenched to 1600, 1200, 600, and 300 K and equilibrated for 160 ps at every temperature, so as to anneal the surface and the interface between the crystalline and the amorphous regions.

Figure 1 shows the ratio between the computed thermal conductivity of bulk Si and SiNWs, as a function of the diameter. The most notable features are the dramatic dependence of κ on surface structure, and its 10- and 100-fold reduction in the case of square cross sections, and of rough, amorphized surface layers, respectively. No definite trend of κ as a function of size is observed, except for a clear increase up to bulk values for pristine, crystalline wires with $d \approx 1$ nm. Large values of κ in very thin wires were reported also in Ref. [10], and reflect the tendency of

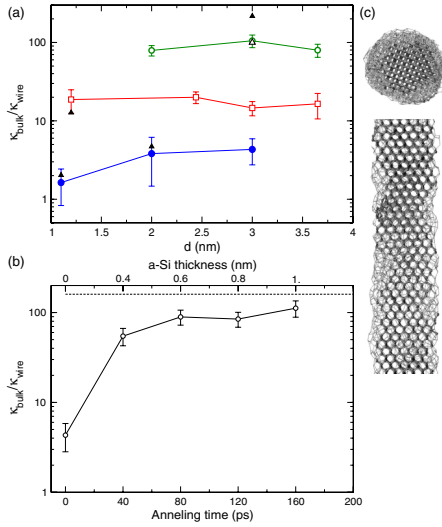


FIG. 1 (color online). Ratio between the thermal conductivity of bulk silicon and that of thin silicon nanowires at room temperature, as a function of the diameter (a), and of the thickness of the amorphous shell for the 3 nm thick wire with crystalline core-amorphous shell structure (b), as obtained in our atomistic simulations. In panel (a), filled circles refer to crystalline nanowires, squares to nanowires with square cross section, and empty circles to crystalline core-amorphous shell wires. Filled triangles refer to BTE calculations, and the empty one is the result of combining BTE with the Allen-Feldman theory for core-shell SiNW. In our calculation, surface amorphization is controlled by the duration of thermal annealing cycles applied to crystalline wires at a temperature close to the melting temperature of bulk Si. The dashed line in (b) indicates the thermal conductivity of amorphous silicon. In panel (c), a core-shell SiNW with a diameter of 3 nm is sketched.

the system to approach the conditions of an ideal one-dimensional heat conductor, for which κ is known to diverge with system size [23]. Our results show that at variance with heat transport in thicker SiNW ($d > 50$ nm), in thin wires, phonon confinement through dimensionality reduction [7,8] does not necessarily lead to low values of κ ; on the contrary, long wavelength modes present in quasi-one-dimensional systems may give rise to values of κ comparable to those of bulk Si. Therefore, a theory of heat conduction which approximates the phonon mean free path by wire diameter [8] is not predictive in the size range considered here.

Figure 1(b) reports the dependence of the thermal conductivity of core-shell SiNWs with $d = 3$ nm, as a function of the thickness of the amorphous shell. It is seen that the formation of a disordered surface as thin as two atomic layers is sufficient to reduce κ by an order of magnitude with respect to that of crystalline wires with the same d . Additional amorphization reduces κ further, and eventually its value approaches that of bulk *a*-Si. It is interesting to note that the presence of an amorphous shell as thin as 0.6 nm makes κ drop to values that may prove to be appealing for thermoelectric applications, provided the electronic conductivity and power factor of the crystalline

core are not significantly altered by the presence of the amorphous shell layer [24]. Even though calculations on pure crystalline and rough wires have shown that the electronic conductivity is very sensitive to surface passivation and disorder [6,25,26], experiments on *a*-SiO₂ passivated SiNW indicate that the power factor is much less sensitive to surface roughness than κ [1]. Explicit calculation of S and σ in core-shell SiNW will be necessary to draw definite conclusions.

Hereafter, we aim at elucidating the effects induced by surface amorphization by using a parameter-free model. We note that theories of heat transport in rough wires in the quantum regime have been developed; however, they have been either restricted to low temperatures and coherent processes [27], or they require fit of empirical parameters [28,29]. In a recent work on Carbon Nanotubes [18], we have shown that an approach based on the BTE, in which phonon relaxation times are computed directly from MD simulations, yields results for the thermal conductivity in excellent agreement with MD. In addition, such an approach allows one to analyze in detail the contribution (κ_i) to κ of each phonon mode. Within the single mode relaxation time approximation [30], κ_i is given by

$$\kappa_i(\mathbf{q}) = C_i(\mathbf{q})v_i^2(\mathbf{q})\tau_i(\mathbf{q}), \quad (1)$$

where $v_i(\mathbf{q})$ and $\tau_i(\mathbf{q})$ are the group velocities and the lifetimes of the phonon mode with momentum $\mathbf{q}$, respectively. $C_i(\mathbf{q})$ is the specific heat per unit volume of each vibrational state, using the Bose-Einstein statistics. Results from the BTE are shown in Fig. 1 by the full triangles, where it is seen that good agreement with MD is obtained for crystalline wires (BTE results obtained using the Boltzmann or Bose-Einstein statistics for C_i differ by less than 2% at $T = 300$ K). BTE results are however substantially smaller (more than 50%) than MD values for core-shell wires, and we will show below that in the latter case, specific treatment of heat carriers in the presence of atomic disorder is required [21,31], in order to understand the main contributions to κ .

The average lifetimes τ of the vibrational modes of several SiNWs are shown in Fig. 2(a). Lifetimes are computed as the decay exponent of the modes amplitude autocorrelation function obtained from equilibrium MD in the microcanonical ensemble. While in bulk systems the phonon lifetimes scale as $1/\omega^2$, here different behaviors are observed, depending on the surface structure. Shape and surface geometry do not significantly affect the magnitude of τ of crystalline wires, over the entire frequency range. In particular, several vibrational modes with long lifetimes are present in the low frequency part of the spectrum in both round and square crystalline SiNW. Therefore, lifetime values may not be responsible for the 10-fold difference in κ of crystalline wires with different cross sections. These variations are instead determined by the group velocities [Fig. 2(b)] that, in square wires, due to the presence of surface defects (e.g., kink) are on average significantly

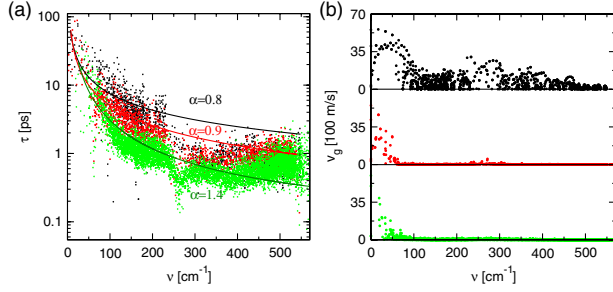


FIG. 2 (color online). Computed relaxation times (a) and group velocities (b) of the vibrational modes of a 1.1 nm crystalline nanowire (black), 1.2 nm square cross section nanorod (red), and a 3 nm core-shell nanowire with 1 nm thick amorphous shell (green). Solid lines indicate the fitting of τ to $1/\omega^\alpha$.

smaller than in pristine, crystalline wires. The presence of residual surface defects in square nanorods is indeed the main cause for the observed reduction of the group velocities and thus for the drop of κ . On the other hand, vibrational lifetimes in core-shell nanowires are on average 1 order of magnitude lower than those of their crystalline counterpart. However, given the linear dependence of κ on τ , the computed relaxation times do not fully account for the observed drop of κ in the presence of surface disorder.

We note that Eq. (1) may be used to compute the contribution to κ only of propagating vibrational modes. Yet, in disordered systems, e.g., *a*-Si and *a*-SiO₂, most of the vibrational modes do not have a well defined polarization and cannot be properly assigned a group velocity. Although such modes do not propagate as phonons in crystals, they are in general extended, they may have finite diffusivity, and thus carry heat [31].

Figure 3(a) shows the participation ratios computed for vibrational modes of core-shell SiNWs with $d = 3$ nm and different thicknesses (t) of the surface amorphous layer. The graphs show that even in the case of heavily amorphized SiNW ($t \sim 1$ nm), vibrational modes do not undergo significant localization. Only high-frequency ($\nu > 530$ cm⁻¹) optical modes are localized on less than 100 atoms, while an analysis of the polarization vectors (not shown) and the direct calculation of group velocities shows that modes with frequency (ν) > 70 cm⁻¹ do not propagate. These properties closely resemble those of the vibrational modes of *a*-Si [31,32], for which a mobility edge was identified at 570 cm⁻¹; in addition, the modes between 50 cm⁻¹ and 570 cm⁻¹ were found to have a diffusive, nonpropagating character. In the case of core-shell SiNW, we can separate the contribution to the total vibrational density of state of the amorphous and the crystalline regions [see Fig. 3(b)]. The two components of the power spectrum nearly overlap at low frequency (< 50 cm⁻¹) but differ significantly elsewhere. While the crystalline core displays an intense peak corresponding to optical modes at 500 cm⁻¹, the amorphous shell contributes a larger amount of modes in the range between 50 and 180 cm⁻¹, and these have a marked diffusive character.

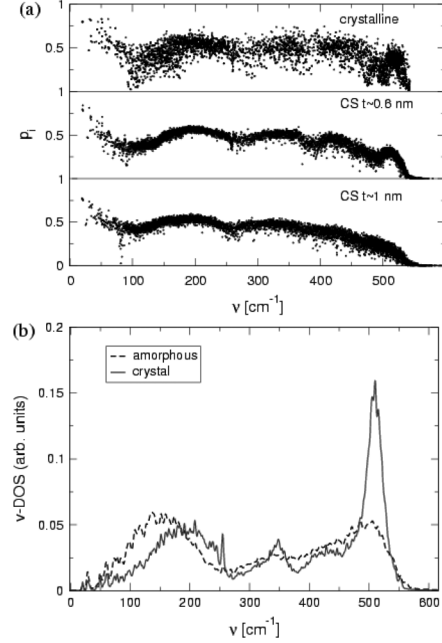


FIG. 3. (a) Participation ratio (p_i) of the vibrational modes of crystalline and core-shell nanowires with 3 nm diameter and different thickness of the amorphous layer. p_i is defined as $p_i^{-1} = N \sum_n [\sum_\alpha e_{\alpha,n}^*(i) e_{\alpha,n}(i)]^2$, where $e_{\alpha,n}(i)$ is the component of the eigenmode i relative to the coordinate α of the atom n , and indicates the fraction of atoms participating in a given mode. (b) Decomposition of the vibrational density of states into the contribution from the crystalline (solid line) and the amorphous (dashed line) region of the core-shell wire with 1 nm thick amorphous layer.

The contribution κ_i to κ of diffusive, nonpropagating modes was computed using the AF theory [21,31] successfully applied to *a*-Si [31,33], where $\kappa_i = C_i D_i$ and the mode diffusivity is given by

$$D_i = \frac{\pi V^2}{\hbar^2 \omega_i^2} \sum_{j \neq i} |\langle i | J_z | j \rangle|^2 \delta(\omega_i - \omega_j). \quad (2)$$

Here, $\langle i | J_z | j \rangle$ is the z component of the heat flux operator projected on the i and j vibrational eigenstates. In core-shell SiNWs, group velocities are essentially zero for frequencies $\nu \geq 70$ cm⁻¹, but the modes at higher frequency have a finite diffusivity (Fig. 4), thus providing a substantial contribution to thermal transport.

In order to quantitatively model the thermal conductivity of core-shell SiNW, we have treated the propagating phonon modes up to 70 cm⁻¹ by using the BTE, while we employed Eq. (2) to compute the contribution to κ of diffusive modes. The calculation is not particularly sensitive to the choice of the crossover frequency between propagating and diffusive regimes, as in the range between 50 and 80 cm⁻¹, $D \sim \nu^2 \tau$, and modes may be properly described by either model. The results obtained in this way are in excellent agreement with those of MD simulations (see Fig. 4): phonon modes account for about half of the

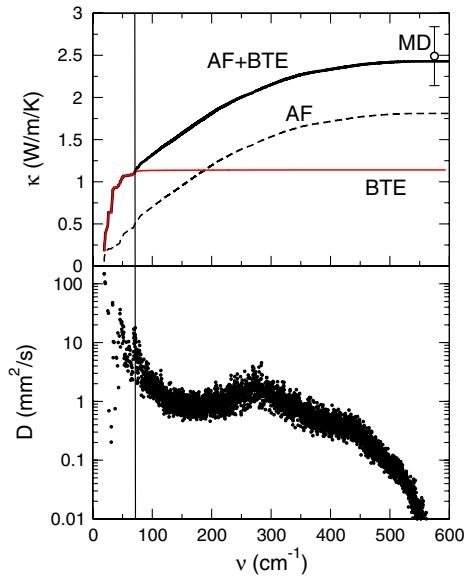


FIG. 4 (color online). Diffusivity of the vibrational modes of a core-shell SiNW with 3 nm diameter and *a*-Si thickness of 1 nm, computed using the model by Allen and Feldman [21] (lower panel). Thermal conductivity of the same core-shell SiNW computed combining the contribution from the Boltzmann transport equation (BTE) for the modes with frequency lower than 70 cm^{-1} (indicated by the vertical line) and the model by Allen and Feldman (AF) for the modes with frequency higher than 70 cm^{-1} (upper panel).

computed value of κ and diffusive but nonpropagating vibrations account for the other half.

In conclusion, we have shown that the thermal conductivity of thin SiNWs ($d \leq 4 \text{ nm}$) is insensitive to variations of the diameter. Size reduction and phonon confinement do not necessarily lead to low values of κ ; on the contrary, in some cases, κ increases as a function of size, due to the presence of long wavelength phonons with very long mean free paths. Values of the ionic thermal conductivity 10 and 100 times lower than in bulk Si may be attained by tailoring the surface structure of the wires. For example, a small amount of disorder in the surface reconstruction of square SiNWs is sufficient to substantially flatten phonon dispersion curves and lead to a 10-fold decrease in κ . In *a*-Si coated SiNWs, a 100-fold drop of κ may be achieved, due to a decrease of propagating mode lifetimes at the crystalline-amorphous interface, combined with the presence of non propagating, diffusive modes similar to those found in *a*-Si. Our results are fully consistent with the experiment reported in Ref. [1] and provide a microscopic explanation for the values of thermal conductivity measured for so called rough wires. Finally, we note that based on our results, we expect alloying at the interface, e.g., of Si with Ge, to further decrease the thermal conductivity of semiconducting wires.

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