

Surface-Decorated Silicon Nanowires: A Route to High- ZT Thermoelectrics

Troels Markussen,¹ Antti-Pekka Jauho,^{1,2} and Mads Brandbyge¹

¹*Department of Micro- and Nanotechnology, Technical University of Denmark, DTU Nanotech, Building 345 East, DK-2800 Kongens Lyngby, Denmark*

²*Department of Applied Physics, Helsinki University of Technology, P.O. Box 1100, FIN-02015 HUT, Finland*
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Based on atomistic calculations of electron and phonon transport, we propose to use surface-decorated silicon nanowires for thermoelectric applications. Two examples of surface decorations are studied to illustrate the underlying ideas: nanotrees and alkyl functionalized silicon nanowires. For both systems we find (i) that the phonon conductance is significantly reduced compared to the electronic conductance leading to high thermoelectric figure of merit ZT , and (ii) for ultrathin wires, surface decoration leads to significantly better performance than surface disorder.

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Recent ground-breaking experiments indicate that rough silicon nanowires (SiNWs) can be efficient thermoelectric materials although bulk silicon is not [1,2]: They conduct charge well but have a low heat conductivity. A measure for the performance is given by the figure of merit $ZT = G_e S^2 T / \kappa$, where G_e , S , and T are the electrical conductance, Seebeck coefficient, and (average) temperature, respectively. The heat conduction has both electronic and phononic contributions: $\kappa = \kappa_e + \kappa_{ph}$. Materials with $ZT \sim 1$ are regarded as good thermoelectrics, but $ZT > 3$ is required to compete with conventional refrigerators or generators [3]. Recent theoretical works predict $ZT > 3$ in ultrathin SiNWs [4–6]. The high performance SiNWs in Ref. [1] were deliberately produced with a very rough surface, and the high ZT is attributed to increased phonon-surface scattering which decreases the phonon heat conductivity, while the electrons are less affected by the surface roughness. The extraordinary low thermal conductivity measured in rough SiNWs is supported by recent calculations [7,8]. Surface disorder will, however, begin to affect the electronic conductance significantly in very thin wires [9] and thereby reduce ZT [5,6].

For defect-free wires, the room temperature phononic conductance scales with the cross-sectional area [10]. On the contrary, for ultrathin wires with diameters $D \lesssim 5$ nm, the electronic conductance is not proportional to the area: It is quantized and given by the number of valence/conduction band states at the band edges. Decreasing the diameter to this range thus decreases κ_{ph} while keeping G_e almost constant. An optimally designed thermoelectric material would scatter phonons but leave the electronic conductance unaffected, even for the smallest wires. Instead of introducing surface disorder, which affects the electronic conductance in the thin wires, it is interesting to speculate whether other surface designs could lead to improved thermoelectric performance. Lee, Galli, and Grossman [11] proposed nanoporous Si as an efficient thermoelectric material. Blase and Fernández-Serra [12] recently showed that covalent functionalization of SiNW

surfaces with alkyl molecules leaves the electronic conductance unchanged, because the molecular states are well separated in energy from the nanowire band edges; see Fig. 1. If the alkyl molecules scatter the phonons, such functionalized SiNWs would be candidates for thermoelectric applications. Experimental alkyl functionalization of SiNWs was reported in Ref. [13].

Another possible surface design are branched SiNWs, so-called nanotrees. Nanotrees have been synthesized in III-VI semiconductors [14,15] and in silicon [16,17]. The stability and electronic structure of silicon nanotrees have recently been addressed theoretically [18,19]. The thinner

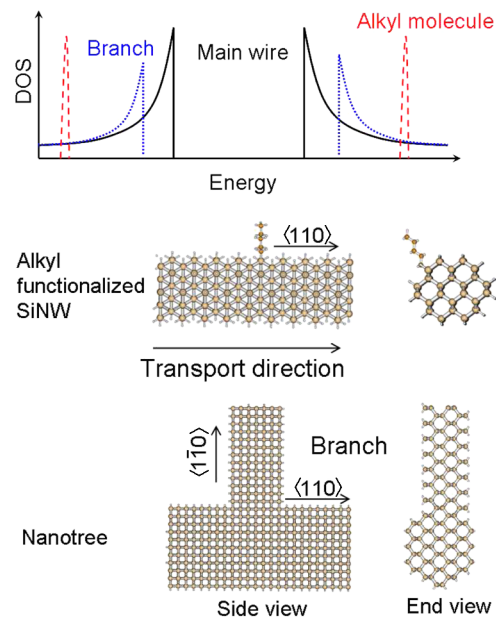


FIG. 1 (color online). Sketch of electronic density of states (top) in the alkyl functionalized SiNW (middle) and in the nanotree (bottom). The trunk in the nanotree is broader than the branch and thus has a smaller band gap. Also, the alkyl molecular states are located deep inside the bands. For both structures, electrons and holes close to the band edges are therefore only weakly scattered while phonons are strongly scattered.

branches will have a larger band gap than the main wire (“trunk”); see Fig. 1. Close to the band edges, the electronic scattering is therefore weak.

The presence of an alkyl molecule or a nanowire branch leads to both a reduction $\Delta\kappa$ of the thermal conductance and a reduction ΔG of the electronic conductance. In this Letter, we show that at room temperature (RT) the ratio $\Delta\kappa/\Delta G > 50$ for the alkyl functionalized SiNWs and $\Delta\kappa/\Delta G > 20$ for a nanotree. By engineering the SiNW surfaces, it is thus possible to reduce the phonon conductance while keeping the electronic conductance almost unaffected. We thus propose such surface-decorated SiNWs as promising candidates for nanoscale thermoelectric applications.

Systems.—We consider two specific systems shown in Fig. 1. The first is an alkyl functionalized SiNW with a wire diameter of 12 Å and with the wire oriented along the $\langle 110 \rangle$ direction. The alkyl (C_nH_{2n+1}) is attached to the H-passivated nanowire replacing a H atom. The second system is a nanotree, where a small diameter (12 Å) branch is attached to a larger diameter (20 Å) trunk. The trunk is oriented in the $\langle 110 \rangle$ direction, while the branch is oriented along the $\langle 1\bar{1}0 \rangle$ direction and is thus perpendicular to the trunk. The length of the branch L_B is varied.

Methods.—The electronic Hamiltonian \mathbf{H} and overlap matrix \mathbf{S} of the alkyl functionalized SiNWs are obtained from local orbital density-functional theory (DFT) calculations [20,21]. The calculations are performed on supercells containing 7 wire unit cells with the alkyl molecule bound to the middlemost unit cell, as shown in Fig. 1.

For the nanotrees, we use a tight-binding (TB) model since these systems contain >1100 atoms, too many for our DFT implementation. The electronic TB Hamiltonian describing the nanotree is calculated using a 10 band $sp^3d^5s^*$ nearest-neighbor orthogonal TB parametrization [22,23]. We recently applied the same TB model to study thermoelectric properties of surface disordered SiNWs [6].

The phononic system, characterized by the force constant matrix \mathbf{K} , is described using the Tersoff empirical potential (TEP) model [24,25] for both the nanotree and the functionalized SiNW. For pristine wires, we have recently shown that the TEP model agrees well with more elaborate DFT calculations [10]. We limit our description to the harmonic approximation, thus neglecting phonon-phonon scattering. The harmonic approximation is always valid at low temperatures. In bulk Si, the room temperature anharmonic phonon-phonon relaxation length at the highest frequencies is $\lambda_a(\omega_{\max}) \sim 20$ nm and increases as $\lambda_a \propto \omega^{-2}$ at lower frequencies [26]. Experimental studies of silicon films [27] showed that the effective mean free path of the dominant phonons at room temperature is ~ 300 nm. For relatively short wires with lengths $L \leq 100$ nm, the anharmonic effects thus seem to be of limited importance, and the harmonic approximation is expected to be good.

We calculate the electronic conductance from the electronic transmission function $\mathcal{T}_e(\varepsilon)$. This is obtained from

the \mathbf{H} and \mathbf{S} matrices following the standard nonequilibrium Green’s function/Landauer setup, where the scattering region (i.e., the regions shown in Fig. 1) is coupled to semi-infinite, perfect wires [28]. The electronic quantities in the ZT formula can be written as [29–31] $G_e = e^2 L_0$, $S = L_1(\mu)/[eTL_0(\mu)]$, and $\kappa_e = \{L_2(\mu) - [L_1(\mu)]^2/L_0(\mu)\}/T$, where $L_m(\mu)$ is given by

$$L_m(\mu) = \frac{2}{h} \int_{-\infty}^{\infty} d\varepsilon \mathcal{T}_e(\varepsilon) (\varepsilon - \mu)^m \left(-\frac{\partial f(\varepsilon, \mu)}{\partial \varepsilon} \right). \quad (1)$$

Here $f(\varepsilon, \mu) = 1/\{\exp[(\varepsilon - \mu)/k_B T] + 1\}$ is the Fermi-Dirac distribution function at the chemical potential μ .

The phonon transmission function $\mathcal{T}_{\text{ph}}(\omega)$ at frequency ω is calculated in a similar way as the electronic transmission with the substitutions $\mathbf{H} \rightarrow \mathbf{K}$ and $\varepsilon \mathbf{S} \rightarrow \omega^2 \mathbf{M}$, where \mathbf{M} is a diagonal matrix with the atomic masses [32–34]. The phonon thermal conductance is

$$\kappa_{\text{ph}}(T) = \frac{\hbar^2}{2\pi k_B T^2} \int_0^{\infty} d\omega \omega^2 \mathcal{T}_{\text{ph}}(\omega) \frac{e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2}. \quad (2)$$

Charge transport.—Figures 2(a) and 2(b) show the calculated hole and electron transmissions for a pentyl (C_5H_{11}) functionalized SiNW. Notably, the transmission is nearly perfect close to the band edges. The average reduction of the transmission in the first hole and electron conductance plateaus is 2% and 0.2%, respectively,

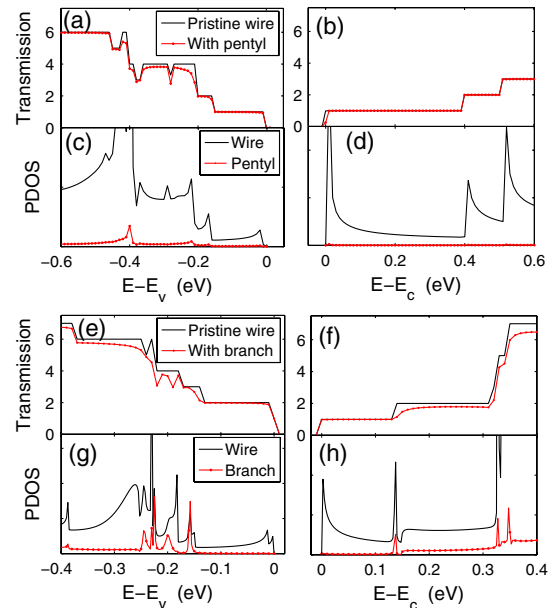


FIG. 2 (color online). Hole and electron transmissions for pentyl functionalized, $D = 12$ Å SiNW (a)–(b) and for a nanotree with branch length $L_B = 15.4$ Å (e)–(f). Panels (c)–(d) and (g)–(h) show the PDOS on the wire and on the pentyl and branch, respectively. The energy scales are relative to the valence band edge E_v for the holes (left column) and relative to the conduction band edge E_c for electrons (right column). The DFT band gap of the $D = 12$ Å wire is 1.65 eV, while the TB band gap of the $D = 20$ Å wire is 1.77 eV.

in agreement with the findings of Ref. [12]. Figures 2(c) and 2(d) show the projected density of states (PDOS) on the wire and on the pentyl. The high transmission regions in panels (a) and (b) are seen to correspond with regions of vanishing PDOS on the pentyl molecule. Likewise, at energies in the valence band where scattering is observed, there is a relatively large PDOS at the pentyl.

Figures 2(e) and 2(f) show the transmission through the nanotree. Again, the transmission close to the band edges is nearly perfect, with a reduction of 2% and 0.9% for holes and electrons, respectively. Figures 2(g) and 2(h) show the PDOS on the main wire and on the branch. We again observe a correspondence between perfect transmission and low PDOS on the branch.

The almost perfect transmissions close to the band edges can be qualitatively understood from the schematic drawing in Fig. 1 (top). The highest occupied molecular orbital and lowest unoccupied molecular orbital level of the pentyl are located deep inside the bands [12], and the molecular states are thus not accessible for electrons or holes close to the band edges. For the nanotree, the branch has a smaller diameter and thus a larger band gap. Electrons or holes in the trunk, with energies close to the band edges, are not energetically allowed in the branch and therefore do not “see” the branch. In addition to the energy considerations, the spatial distribution of the Bloch state also plays a role: The first valence and conduction band Bloch states of the main wire have more weight in the center of the wire than at the edge [6].

Thermal transport.—Figure 3 shows the temperature dependence of the thermal conductance ratios κ/κ_0 , where κ_0 is the pristine wire thermal conductance, which in the low energy limit equals the universal thermal conductance quantum $\kappa_Q(T) = 4(\pi^2 k_B^2 T/3h)$ [35]. Figure 3(a) shows

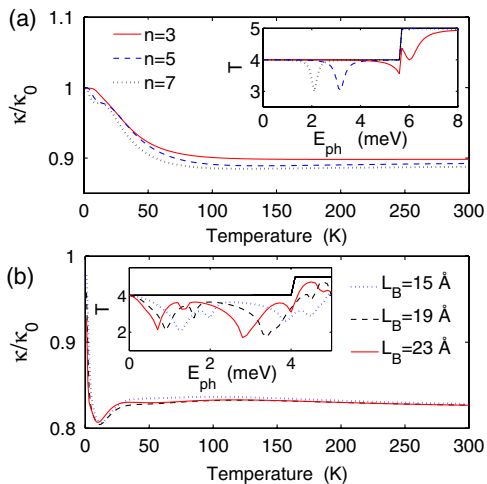


FIG. 3 (color online). Thermal conductance ratio κ/κ_0 (a) for alkyl functionalized SiNWs with different alkyl lengths and (b) for nanotrees with different branch lengths L_B . The nanotree trunks are again $D = 20$ Å with 12 Å diameter branches. The insets show the phonon transmission function at low energies. Fano-like resonant scattering is observed in both systems.

the ratios for wires with alkyls C_nH_{2n+1} , with different lengths $n = 3, 5, 7$. The thermal conductance at RT is reduced by $\sim 10\%$, and the overall behavior does not depend on the alkyl length. The inset shows the phonon transmission at low phonon energies. Note the resonant dips in the transmission, where exactly one channel is closed yielding a transmission of three. These dips are associated with an increased local phonon density of states at the alkyl molecule at the resonant energies, corresponding to a localized vibrational mode. Such Fano-like resonant scattering is well-known from electron transport [36]. A phonon eigenchannel analysis [37] shows that the transmission dips are due to a complete blocking of the rotational mode in the wire. The corresponding localized alkyl phonon mode is a vibration in the plane perpendicular to the wire axis.

Figure 3(b) shows the thermal conductance ratio for nanotrees with different branch lengths L_B . There is only a weak dependence on L_B at low temperatures, and at RT the four curves basically coincide showing a thermal conductance reduction of 17% of the nanotree compared to the pristine wire. Again we observe resonant transmission dips for the nanotrees. Two channels—the rotational and one flexural mode—close completely at the resonance due to two quasilocalized vibrational modes in the branch. These phonon backscattering resonances are responsible for the dip in the κ/κ_0 ratio around $T = 10$ K. Notice that all of the conductance ratios approach unity in the low temperature limit. This is because the four acoustic modes transmit perfectly in the limit $\omega \rightarrow 0$ [35].

We may vary the thermoelectric figure of merit ZT by varying the chemical potential. Typically, ZT displays a maximum for μ close to the band edge [4,6]. Figure 4 shows the maximum ZT values for the pentyl functionalized SiNW (squares), the nanotree (circles), and surface disordered SiNWs (triangles), where disorder is modeled by introducing surface silicon vacancies. The diameter of

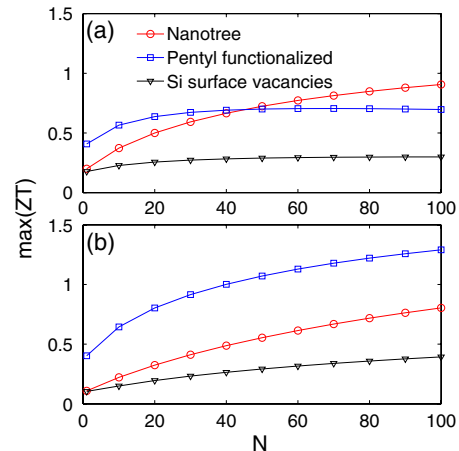


FIG. 4 (color online). Thermoelectric figure of merit ZT for p -type (a) and n -type (b) wires. N is the number of pentyl molecules (squares), nanotree branches (circles), and silicon surface vacancies (triangles) in the wire.

the surface disordered wire is $D = 20 \text{ \AA}$, and it is oriented along the $\langle 110 \rangle$ direction. The calculational details are given in Ref. [6]. The curves show ZT as a function of the number (N) of pentyl molecules/nanotree branches/silicon vacancies. In calculating ZT vs N , we have assumed that the transmission \mathcal{T}_N through a longer wire with, e.g., N pentyl molecules randomly covering the surface can be obtained from the single-pentyl transmission \mathcal{T}_1 as $\mathcal{T}_N^{-1} = \mathcal{T}_0^{-1} + N(\mathcal{T}_1^{-1} - \mathcal{T}_0^{-1})$, where \mathcal{T}_0 is the pristine wire transmission. The term in parentheses corresponds to a scattering resistance of a single pentyl molecule. This averaging method has recently been validated in the quasisballistic and diffusive regimes for both electron and phonon transport [6,38,39].

Figure 4 shows that increasing the number of scattering centers, i.e., the number of pentyl molecules or nanotree branches, increases the ZT for both (a) hole transport and (b) electron transport. In the case of holes in the pentyl functionalized SiNWs, the ZT reaches an almost constant level of $ZT = 0.7$ at $N = 40$, but in all other cases, ZT increases throughout the range. Increasing the density of molecules/nanotree branches or increasing the length of the wire will thus increase the thermoelectric performance. The reason is that the electrons (holes) are less affected by the surface modifications than the phonons, as also seen in Figs. 2 and 3. The surface disordered wires (triangles) show an increasing ZT vs N but at values significantly lower than the two other surface modified wires.

Discussion.—A number of idealizations have been made in our calculations, and we next assess their significance. The structures we have considered represent plausible choices, dictated by computational limitations, but do not necessarily match quantitatively real structures. Thus, for example, a surface-decorated SiNW will also be rough, and one should consider the combined effect of all scattering mechanisms. We have carried out optimizations neither with respect to the attached molecules nor with respect to the geometry of the nanotrees. Electron-phonon and phonon-phonon scattering will affect both the electronic and thermal conductances and the obtained ZT values [5]. We do not expect to reach quantitative agreement with experiment but believe to have identified important trends: In SiNW-based thermoelectrics, surface decorations in terms of added molecules or nanowire branches seem to be a better approach than surface disorder in the ultrathin limit.

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