Prediction of Reduced Thermal Conductivity in Nano-Engineered Rough Semiconductor Nanowires

Pierre N. Martin\textsuperscript{1,2}, Zlatan Aksamija\textsuperscript{1,2}, Eric Pop\textsuperscript{1,2,3} and Umberto Ravaioli\textsuperscript{1,2}

\textsuperscript{1}Department of Electrical and Computer Engineering, \textsuperscript{2}Beckman Institute for Advanced Technology and Science, \textsuperscript{3}Micro- and Nano-Technology Laboratory, University of Illinois, Urbana-Champaign, Urbana, IL 61801, USA

E-mail: pmartin7@illinois.edu, epop@illinois.edu

Abstract. We explore phonon decay processes necessary to the design of efficient rough semiconductor nanowire (NW) thermoelectric devices. A novel approach to surface roughness-limited thermal conductivity of Si, Ge, and GaAs NW with diameter $D < 500$ nm is presented. In particular, a frequency-dependent phonon scattering rate is computed from perturbation theory and related to a description of the surface through the root-mean-square roughness height $\Delta$ and autocovariance length $L$. Using a full phonon dispersion relation, the thermal conductivity varies quadratically with diameter and roughness as $(D/\Delta)^2$. Computed results are in agreement with experimental data, and predict remarkably low thermal conductivity below $1 \text{ W/m/K}$ in rough-etched 56 nm Ge and GaAs NW at room temperature.

Semiconductor nanowires (NWs) have drawn much attention for their potential applications in field effect transistors [1,2], interconnects [2], thermoelectrics [3, 4, 5], and heterostructures [6]. Given their high surface-to-volume aspect ratio, the most prominent size effect limiting transport originates from scattering of carriers with the surface. Recent experimental and theoretical work [4, 7] suggested that potentially high thermoelectric figures of merit $ZT$ could be achieved by scattering phonons more effectively than electrons at the interfaces of rough NW. In particular, thermal conductivity in Si NW with etched rough edges was experimentally reduced by a factor of about 100 in comparison to bulk crystalline Si, to nearly the value of amorphous Si. Indeed, it is expected that vibrations of the crystal lattice interfere with the spatial fluctuations of the NW boundaries. Hence, it is theoretically relevant to adopt a picture where the interference process is stronger in thin NW for a given roughness root-mean-square height (RMS)$\Delta$, and vary with the wavelength of incident phonons and the temperature of the crystal lattice. Nevertheless, most of the work in phonon transport only accounts for surface roughness scattering by a constant fitting parameter which reflects an average probability of diffuse scattering at the NW surface. We recently proposed [7] a perturbative approach to phonon – surface roughness scattering, where a matrix element is derived for such interactions. This model has shown excellent agreement to experimental observations on rough Si NW below 50 nm where the effect of surface roughness is the strongest, yielding $ZT \approx 0.6$. In order to assist the design of efficient thermoelectric NW devices, the present work explores the trade-offs between different scattering mechanisms in Si, Ge, and GaAs necessary to achieve high figures of merit $ZT > 1$.

The roughness of a surface is generally quantified by its RMS height $\Delta$ and auto-correlation length $L$. The present model accounts for the variation of a NW thermal conductivity with the experimentally observable $\Delta$, $L$, and the phonon angular frequency $\omega$; this approach
accurately predicts phonon-surface roughness scattering to contribute to the reduction of thermal conductivity by a factor \((D/\Delta)^2 \omega^{-2}\) where \(D\) is the NW diameter. In addition, the quality of thermoelectric devices is measured by the dimensionless figure of merit \(ZT = (S^2\sigma/\kappa)T\), where \(S\) is the Seebeck coefficient, \(T\) the temperature, \(\sigma\) the electrical conductivity and \(\kappa\) the thermal conductivity. With this respect, a standard approach to achieve performance is to design a “phonon glass - electron crystal”, with high electron mobility and poor thermal conductivity. Among those thermally resistive mechanism in a semiconductor crystal, scattering of phonons by isotopes or in three-phonon anharmonic decays is also of considerable importance.

Our model assumes that no phonon is emitted in the surrounding environment. This condition reflects the case where NW are wrapped in a medium of considerably different \(\kappa\), as it is for semiconductor NW wrapped in oxide or suspended in vacuum. While propagating along wires of diameter \(D < 500\) nm, phonons scatter from a series of constriction along the transport direction which result from the surface asperities and are reflected by a perturbed Hamiltonian \(H'\) of the system. The interface roughness is considered as a space varying dilatation \(\delta(r)\) of the wire, which auto-correlation function is assumed to be exponential \(\Delta(r) = \Delta \exp(-r/L)\). Following the derivation of Klemens [8], the matrix element for a perturbation due to a space varying dilatation reflects the transitions of phonons from a state of momentum \(k\) to \(k'\) such as

\[
|\langle k | H' | k' \rangle|^2 = \frac{4\gamma^2}{3V_{cd}} \omega^2 \langle n' \rangle \Delta(k - k')
\]

where \(V_{cd}\) is the volume of the device, \(\gamma\) is Grüneisen’s parameter, \(\omega\) is the angular frequency of the incident phonon, and \(\Delta(q) = \pi \Delta^2 L^2 \exp(-L^2 q^2/4)\) is the roughness power spectrum associated to \(\Delta(r)\). Close to equilibrium, the occupation of the destination phonon branch \(\langle n' \rangle\) is given by the Bose-Einstein distribution and reflects the temperature dependence of the model \(\langle n' \rangle = (\exp(h\omega/k_BT) - 1)^{-1}\). The probability of transitions from \(k\) to \(k'\) due to surface roughness is directly proportional to the matrix element derived above. As a consequence of the \(\omega^2\) factor, low frequency phonons experience little thermal resistance from surface asperities. In addition, the dependence on the autocorrelation length \(L\), which represents the average width of roughness peaks, shows that smoothly varying surfaces favor scattering events of the specular type.

We use a Gilat-Raubenheimer (GR) [9] scheme to compute the surface roughness scattering

**Figure 1.** (a) Phonon – surface roughness scattering rates computed at room temperature in Si, Ge, GaAs. (b),(c),(d) Computed full phonon branches in the FBZ of Si, Ge, and GaAs respectively. Dots are extracted from experimental observations [10, 11] for comparison. \(L = 22\) Å throughout.
Figure 2. Effect of NW diameter on thermal conductivity for varying roughness RMS in (a) Si [7], (b) Ge, and (b) GaAs. \( L = 22 \) A throughout.

rate integrals in Si, Ge, and GaAs (see Fig. 1.a)

\[
\tau^{-1}_{i,j}(E) = \frac{2\pi}{\hbar N_i(E)} \int_{E_i=H} \frac{|\langle k|H'|k'\rangle|^2}{\nabla_k E'(k')} \, dS \tag{2}
\]

where \( \tau^{-1}_{i,j} \) is the transition rate from phonon branch \( i \) to \( j \) due to surface roughness and \( E'(k) \) is the phonon dispersion relation on the destination branch \( j \). In order to account for the frequency dependence of phonon-surface roughness interference process, full dispersion relations are used, which are obtained from an adiabatic bond charge model, and approximate the dispersion relations observed in Si, Ge and GaAs [10, 11] with a 1-2.5% error (Fig. 1.b, c, d).

The latter surface roughness scattering rate is added to the total scattering rate by Mathiessen’s rule. Subsequently, we compute thermal conductivity in Holland’s formalism [12]

\[
\kappa = \frac{\hbar^2}{6\pi^2k_BT^2} \sum_i \int \omega_i(q)\tau_i^{tot}(q) \frac{\exp(h\omega_i/k_BT)}{(\exp(h\omega_i/k_BT) - 1)^2} \, dq \tag{3}
\]

where \( i \) goes over all incident transverse and longitudinal branches, and the wave vector \( q \) models conduction in the NW along the \( \Gamma-(\Delta)-X \) direction. Computations of \( \kappa \) include boundary, isotope, 3 phonon Umklapp, and normal decay processes. Parametric laws are used for the latter rates as described in [7], which are fitted to best reflect experimental bulk \( \kappa \) values [12, 13]. Isotope concentrations of group IV semiconductors match their natural occurrence, with 92.2 \% of \( ^{28} \text{Ge} \), and noticeably only 36.5 \% of \( ^{74} \text{Ge} \) [13]. As a result of its heavier atomic mass and high natural isotope concentration, Ge shows lower \( \kappa \) throughout all simulations (Fig. 2 and 3).

In Fig. 2 and 3, NW thermal conductivity is predicted to decrease in rough nanowires (high RMS\( \Delta \)). The \((D/\Delta)^2 \) behavior is apparent in thin NW of diameter \( D < 115 \) nm, showing that phonon–surface roughness scattering is the dominant resistive process in this case. For intermediate diameters \((D/\Delta \approx 100) \) for Ge and GaAs, 50 for Si, current experiments [4] report \( D = 22 - 115 \) nm and \( \Delta = 0.3 - 5 \) nm), the linear dependence in the diameter suggests that phonons dominantly decay from classical boundary scattering \( \tau_B^{-1}(q) = \nu_s/D \), with \( \nu_s \) the average speed of sound in each branch. For wider \( D \), \( \kappa \) converges to its bulk value.

Low NW thermal conductivity results from the combination of all concurrent interference processes mentioned above. In particular, the effect of artificially high \( \Delta \) and low \( D \) decreases thermal conductivity below 1 W/m/K in Ge and GaAs NW of diameter \( D = 56 \) nm. At this scale, fabrication of rough etched NW remains feasible [4], and the perturbative approach holds validity as the ratio\( \Delta /D \) is only of a few \%, showing good agreement with experimental results (Fig. 3.b). Noticeably, the best fit for the natural Ge sample shows strong isotope and weak Umklapp scattering. As a result, Ge experiences the starkest influence from surface roughness.
at high temperatures, making it a suitable candidate for design of rough NW thermoelectric devices. Our model further predicts weak interference between low energy phonons and surface asperities. Consequently, we noticed very little variation of thermal conductivity with respect to the roughness RMS at temperatures below 100 K.

In summary, we modeled the thermal properties of artificially rough Si, Ge and GaAs NW for thermoelectric applications based on a perturbative treatment of the interaction between lattice vibrations and surface asperities. This approach, based on a full phonon dispersion, accurately accounts for the frequency dependence of phonon scattering processes resulting from surface roughness, isotope, boundary, and anharmonic decays. Our model predicts $\kappa \propto (D/\Delta)^2$ for thin NW, yielding remarkably low thermal conductivity in rough etched Ge and GaAs NW of diameter $D < 115$ nm, thus revealing those materials as potential candidates for efficient thermoelectric devices. Similar scattering mechanisms nevertheless limit electron mobility, making it necessary to model charge transport in order to find optimal thermoelectric figures of merit $ZT$. In this scope, it is noticeable that isotopes have no influence on electronic conduction, and surface roughness may only have limited impact at low $D$ where electrons tend to be pushed away from the interface. Hence, those two factors are expected to be major design axes in the engineering of efficient semiconductor NW thermoelectric devices.

This work was supported in part by the DARPA through the IMPACT Center for Advancement of MEMS/NEMS VLSI grant n. HR0011-06-1-0046 (PM), the DOE Computational Science Graduate Program of the OSNNSA under contract DE-FG02-97ER25308 (ZA), and the Nanoelectronics Research Initiative (NRI) SWAN center (EP).

References

[1] Singhan N, Agarwal A, Bera L, et al. 2006 IEEE Electron Dev. Lett. 27 383.
[2] Steinhog W 2005 Appl. Phys. Lett. 97 023706.
[3] Li D et al. 2003 Appl. Phys. Lett. 83 2934.
[4] Hochbaum A, Chen R, Delgado R, et al. 2008 Nature 451 163.
[5] Ramayya E, Vasileksa D, Goodnick S, et al. 2008 8th IEEE Conference on Nanotechnology 339 (2008).
[6] Dames C and Chen G 2004 J. Appl. Phys. 95 682.
[7] Martin P, Aksamija Z, Pop E and Ravaido U 2009 Phys. Rev Lett. 102 125503.
[8] Klemens P 1958 Solid State Phys. 7 1.
[9] Gilat G and Raubenheimer L 1966 Phys. Rev. 144 390.
[10] Strausch D and Dorner B 1990 J. Phys. Cond. Mat. 2 1457.
[11] Nilsson G and Nelin G 1972 Phys. Rev. B 6 3777.
[12] Holland M 1964 Phys. Rev. 134 471.
[13] Asen-Palmer M et al. 1997 Phys. Rev. B. 56 9431.