Thermal Conductivity of Silicon Nanowire Arrays with Controlled Roughness

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Silicon has historically been considered an inefficient material for thermoelectric energy conversion due to its exceptionally high thermal conductivity. However, most of the heat in Si is carried by phonons with mean-free-path (MFP) larger than 300 nm.\textsuperscript{[1, 2]} For comparison, the MFP of electronic carriers is \approx 10 nm for a $n$-type carrier density of $10^{19}$ cm$^{-3}$.\textsuperscript{[3]} Thus, the thermal conductivity of Si may be reduced without reducing the mobility of charge carriers by utilizing boundaries distributed on nanometer length-scales. Nanowires,\textsuperscript{[4]} thin films,\textsuperscript{[5, 6]} nanomeshes,\textsuperscript{[7, 8]} and polycrystals\textsuperscript{[9]} have each been shown to be effective methods of reducing thermal conductivity when characteristic dimensions fall into the nanoscale regime.
Competitive thermoelectric materials must possess a figure-of-merit, $ZT = S^2\sigma T / \kappa$, on the order of unity. For Si at room temperature, this requires that the lattice thermal conductivity be $\approx 1$ W/m-K. Even ignoring the negative effects of boundaries on electronic properties, the Casimir calculation\cite{10, 11} for boundary-scattering dominated heat conduction indicates that small feature sizes ($\sim 2$ nm) should be required to make Si a viable thermoelectric; the room temperature thermal conductivity of amorphous Si itself is $1.6 - 4$ W/m-K depending on the method of preparation.\cite{12, 13}

Hochbaum et al.\cite{14} have reported measurements of suspended individual nanowires that show additional reductions may be achieved by roughening the surface of the nanowires, with a 52 nm diameter wire achieving a low thermal conductivity of 1.6 W/m-K. Since the origin of the reduction is not currently understood, the ultimate limits of this approach are also not clear. More recently, Hippalgoankar et al.\cite{15} used electron beam lithography (EBL) to define roughness on the outer edge of a suspended wire, and found the thermal conductivity was reduced more modestly ($\sim 30\%$ below the Casimir limit), which they attributed to the different correlation lengths of roughness between EBL-grown nanowires (where the correlation length is $>130$ nm) and nanowires prepared by electroless etching (EE) (correlation length\cite{15} $\sim 60$ nm) such as those of the original report.\cite{14}

Theoretical approaches to understand this initial report are in disagreement over whether reduction below the Casimir limit can happen and also over the physics responsible.\cite{16-19} While two theoretical studies\cite{16, 17} claim good agreement with the published data, they disagree on the mechanism. Molecular dynamics simulations\cite{18, 19} are limited to wires of diameters much smaller than the measured ones. The authors of Ref. 19 conclude\cite{19} that a reduction of thermal conductivity significantly below the Casimir limit requires roughness greater than 20% of the wire diameter even in wires 4 nm in diameter. While the picture remains inconclusive, the unifying theme in a majority of the theoretical effort is
consideration of wave-like phonon transport, otherwise neglected in traditional particle relaxation-time approaches.

In the current paper, we use time domain thermoreflectance (TDTR) to experimentally study the thermal properties of arrays of vertically-aligned Si nanowire with controlled roughness. TDTR has several advantages over the conventional approach of measuring a single nanowire using microfabricated test platforms: (1) Since the nanowires remain integrated to the substrate, the potential for nanowire damage by the scraping process is minimized; (2) A large number of nanowires are sampled during each experiment, typically ~10,000; (3) No microfabrication or micromanipulation is required, greatly expediting the measurement process; (4) The formation of good thermal contacts is greatly simplified, and the thermal interface conductance is easily measured.

Fabrication of roughened Si nanowire array is accomplished by a recently developed two-step wet etch technique, which will be published in detail elsewhere, but the most important aspects are described here. The process begins with a lightly P-doped Si wafer ($\rho$~10 $\Omega$-cm) with a layer of native oxide. A thin layer of Ag (~10 nm as measured by a calibrated quartz crystal monitor) is then deposited by e-beam evaporation and subsequently annealed at 350°C for 4 h under 3-8 x 10^{-7} Torr pressure which thermally dewets the Ag, forming truncated spherical particles (contact angle >90°) on the surface. The size of the particles and the inter-particle spacing depend on the thickness of the Ag as well as the annealing temperature and time; the conditions described above generated particles with average diameter ~100-150 nm. The particles are used as a shadow mask to form a gold mesh (10 nm Au deposited by e-beam evaporation). The removal of Ag particles and lift-off of excess Au is achieved by sonicating the samples in a selective etchant $(\text{NH}_4\text{OH}(32\%):\text{H}_2\text{O}_2(30\%):\text{methanol} = 1:1:2; \text{v:v:v})$. The remaining Au mesh is used as catalyst for a highly anisotropic metal-assisted chemical etch (MacEtch), composed of HF(49\%):H$_2$O$_2$(30\%):ethanol = 13:2:19 (v:v:v). Nanowires arrays were etched to be between
500 nm-1200 nm in length (~2 min. etch). Under these conditions, tapering, which depends on the HF:H$_2$O$_2$ ratio and ethanol concentration, is minimized and typical rms variation of the nanowire length is only ~2-4% of the total length. The Au mesh was subsequently removed using a 90 sec aqua regia etch.

The as-synthesized vertical nanowire arrays were smooth with roughness between 0-1 nm rms, and the area fraction of all arrays was between 17%-29%. To independently introduce roughness, a 6-8 nm layer of Au was deposited by sputtering using a rotating and tilting (0 - 30° with random movement) sample holder, to form nanoscale islands on the sidewalls of the nanowires. A dilute MacEtch solution composed of HF(49%):H$_2$O$_2$(30%):H$_2$O = 1:1:24 (v:v:v) was then used to controllably generate roughness, with the etch time determining the final degree of roughness (figure 1). The roughened samples (∼4 cm$^2$ each) were split in two, with one sample being used for HRTEM roughness characterization and the other for TDTR measurements.

To create a smooth surface suitable for TDTR measurements, a commercially available spin-on glass (SOG), (Filmtronics, Siloxane 500F) was spin coated into the nanowire arrays such that the SOG was slightly thicker than the nanowires. The SOG was then reactively ion etched in CHF$_3$ until the thickness of the SOG is within about ∼20 nm of the nanowire as verified in side view SEM for each sample. Samples were then coated in ~70 nm Al by magnetron sputtering (with precise thickness (+/-4 nm) determined by picosecond acoustics for individual samples). The reflectivity of each sample was compared to a reference sample of a smooth, oxidized Si wafer coated by Al, and all reported samples display specularity greater than 90%, but with most being indistinguishable from the smooth Al reference sample to within experimental uncertainty.

Time domain thermoreflectance was used to characterize the thermal conductivity of the roughened Si nanowire arrays. Our measurement system and methods of data reduction have been described in detail previously.[25, 26] However, for nanowire arrays embedded in a
host matrix material there are several unique aspects to the data acquisition and reduction. Koh et al.\textsuperscript{[27]} have previously reported that thin film composites of vertically aligned InAs nanowire arrays with PMMA matrix filler display effective properties that depend on the modulation frequency, and an effective thermal interface conductance well-below any known physical interface. We observe this to be true for the current Si nanowire arrays as well (figure 2a). Low effective thermal interface conductance is due to the fact that most of the heat is channeled through the nanowire which, due to the low area fraction, amplifies its effective interface resistance by an amount, $\sim 1/x$, where $x$ is the area fraction of nanowires. In the current study, effective thermal interface conductances are observed to be between 25-40 MW/m$^2$K, consistent with a 20-30% areal fraction of nanowires.

The frequency-dependence of the composite thermal conductivity can be understood by examining the origin of the out-of-phase signal in TDTR. The out-of-phase signal depends sensitively on the surface temperature response to a sinusoidal heat input at the modulation frequency;\textsuperscript{[26]} at high modulation frequency, the diffusion distance for heat in the matrix material is much smaller than the distance between adjacent nanowires. Thus, temperature is not uniform in the lateral direction except at the surface, where the array is connected by a high thermal conductivity metal. In this limit, the heat flux divides such that that the average response at the surface is indistinguishable from an effective medium with effusivity,

$$\sqrt{\kappa C_{\text{eff}}} = x\sqrt{\kappa C_{\text{wire}}} + (1-x)\sqrt{\kappa C_{\text{SOG}}}$$

However, at low frequency, heat fully penetrates the matrix material in the lateral direction, so that the temperature is roughly isothermal in-plane. In this case, the surface temperature response is indistinguishable from that of an effective medium with

$$C_{\text{eff}} = xC_{\text{wire}} + (1-x)C_{\text{SOG}}$$

$$\kappa_{\text{eff}} = x\kappa_{\text{wire}} + (1-x)\kappa_{\text{SOG}}$$
In the intermediate frequency range, the behavior cannot be captured by a simple effective medium model. Transient finite element analysis is capable of modeling the intermediate cases; however, performing the simulation of TDTR data requires a summation over the frequency response at thousands of frequencies for each time-delay curve,\(^{[26]}\) which was not practical. Rather, finite element calculations were used only to verify that the transition from the high to low frequency regime is controlled by the thermal diffusion distance in the spin-on-glass compared to the nanowire spacing, and that at the lowest experimental frequencies, the frequency response is well-represented by the effective medium theory in equations 2 & 3.

The measurements at either modulation frequency limit can be used as a simple way to determine the thermal conductivity of the nanowires, \(\kappa_{\text{wire}}\). In the current work, the low frequency limit is used since it is sensitive to the properties deeper within the nanowire arrays and is less sensitive to knowledge of the matrix properties. This requires that the properties of the filler SOG be known; the properties of a pure SOG film (220 nm) were measured at two modulation frequencies (1.6 MHz and 9.8 MHz) to separately determine the thermal conductivity (0.36\(\pm\)0.3 W/m-K) and specific heat capacity (1.3\(\pm\)0.1 MJ/m\(^3\)-K); the thermal conductivity is close to previously measured spin-on-glass with similar composition (\(\sim\)0.38 W/m-K),\(^{[28,29]}\) and the specific heat capacity is near that of other siloxanes such as PDMS (1.3-1.5 MJ/m\(^3\)-K).\(^{[30]}\)

From the low frequency limit of the composite thermal conductivity, the thermal conductivity of the nanowires is then extracted using equations 2 & 3. The extracted values are plotted in figure 2b. The error-bars for the measurement are larger than typical for TDTR measurements (\(\sim\)20\% instead of \(\sim\)10\%)\(^{[31]}\) for several reasons; in addition to the usual error contributions coming from uncertainty in the transducer thickness and heat capacity (\(\sim\)8\% together),\(^{[31]}\) there is uncertainty in the nanowire length (\(\sim\)10\%), the areal fraction of nanowires (\(\sim\)10\% uncertainty based on SEM images at various locations on the chips), and a significant error in the phase of the reference channel due to the lower signal-to-noise ratio.
and smaller jump in the in-phase signal at zero time delay that occurs at low frequency\textsuperscript{[31]} (up to 10% in some cases).

After uncertainties are taken into account, nanowire arrays with low roughness have the highest thermal conductivity, albeit slightly below what has been observed in the case of a similarly-sized nanowire grown by a vapor-solid-liquid (VSL) process and reported previously.\textsuperscript{[4]} Previously measured VLS nanowires all have been [111] oriented, whereas in the current study [100] oriented wire were produced, due to the orientation of the starting wafer. In the Casimir regime, the thermal conductivity of [111] oriented wires are expected to be \(~50\%\) smaller than [100] wires, due to phonon focusing effects;\textsuperscript{[10]} however, comparing the current data to the single nanowire measurement of Li et al.,\textsuperscript{[4]} that behavior was not observed. In qualitative agreement Hochbaum et al.,\textsuperscript{[14]} several highly roughened nanowire arrays are observed with thermal conductivity well below what is explainable from boundary scattering from the nanowire sidewalls (figure 3), with our lowest measured values near 10 W/m-K.

In figure 3b, we have adopted the model developed by Morelli\textsuperscript{[32]} to predict the expected thermal conductivity. The basic elements of the model are that: (1) it is a modified version of the Callaway model;\textsuperscript{[33]} (2) phonon dispersion is treated as isotropic and linear with an energy cutoff determined by the maximum energy of the acoustic branch rather than a Debye frequency; (3) three distinct polarizations are treated; (4) mode-dependent scattering rates are calculated using Matthiessen’s rule, considering normal and umklapp phonon-phonon processes, isotope scattering, and boundary scattering where the boundary scattering length is taken as the diameter of the nanowire in our case. The model implicitly neglects anisotropic effects such as phonon focusing and conduction by optical phonons, but correctly predicts the thermal conductivity of individual Si nanowires measured by Li et al..\textsuperscript{[4]} Comparing our experimental results to the predicted values for nanowires in this size range, the lowest thermal conductivities measured are about 4 times lower than would be expected.
We have characterized the surface features of nanowires using the height-difference correlation function, and this has been compared to the measured thermal conductivity. The height difference correlation function (HDCF), defined as \( G(\rho) \equiv \left\langle (h(x + \rho) - h(x))^2 \right\rangle \), is a real space statistical measurement that gives detailed information about the length scales of the system; in the current context, we use the HDCF to characterize the rms amplitude of roughness (\( \sigma \)) and determine its correlation length (\( \xi \)). The key features of the HDCF are that, typically, for \( \rho < \xi \), \( G(\rho)^{1/2} \approx \rho^{h} \) and approaches a constant \( G(\rho)^{1/2} = \sqrt{2}\sigma \) when \( \rho > \xi \). (For a morphology dominated by a single length scale, \( h \approx 1 \).) The correlation length can be estimated by the intersection of fits to these two regimes, where \( \rho_c = \xi / 4 \). The correlation lengths for all nanowires are in a range from 15-40 nm which is characteristic of the size of the Au islands used during the roughening process (figure 3). Based on the limited range of correlation lengths produced, we cannot determine if there is any dependence of the thermal conductivity on correlation length (figure 3b). The thermal conductivity of our samples do correlate with rms roughness, \( \sigma \) (figure 3c). However, it is difficult to distinguish whether the roughness is the origin of the reduced thermal conduction, or rather if there are other microstructural changes that are associated with the etching process.

Therefore, Raman scattering was employed to gain more insight into the microstructure of the arrays. Numerous studies document Raman scattering from bulk Si,\(^{34}\) amorphous Si,\(^{35}\) and various nanostructured intermediates such as nanocrystals,\(^{36-38}\) porous Si,\(^{39}\) and nanowires.\(^{40, 41}\) For bulk Si in the backscattering geometry, the primary feature of the Raman signal is a sharp peak occurring near 520 cm\(^{-1}\) generated by the zone-center LO phonon, with intrinsic full-width at half-maximum (FWHM)\(^{34}\) ~2.6 cm\(^{-1}\) corresponding to an energy relaxation timescale of ~2.1 ps.\(^{42}\) In nanostructures, the momentum selection rules for scattering are relaxed such that phonons with wavevector \( q \sim 1/L \) also contribute,\(^{38}\) where \( L \) is the characteristic size of the structure. This relaxation of selection rules has the effect of
broadening the energy spectrum of Raman-active phonons and slightly lowering the average energy of the first-order scattering peak. However, in nanowires with diameter >100nm the effect of phonon confinement is expected to be small, with less than 0.02% change in broadening in the linewidth and less than 0.01 cm\(^{-1}\) red-shift in the peak location.\(^{[41]}\)

Despite this expectation, the Raman intensity of our nanowire arrays do show significant broadening and a blue-shift in the peak location that increases with etch time of the roughening process (figure 4). In addition, we see that the thermal conductivity of the nanowire arrays only have low values when their associated linewidth is broadened (figure 4d). The Raman intensities are not fully consistent with phonon confinement in nanostructures, which would be expected to have red-shifted peak locations, unless a large compressive stress is also present. Based on previous measurements of silicon under uniaxial compressive stress that show a blue-shift of \(~0.004\) cm\(^{-1}\)/MPa,\(^{[43]}\) we estimate that the approximate magnitude of the associated stress would need to be \(~300\) MPa. In addition, the length-scales indicated by the classical Raman phonon confinement model\(^{[41]}\) appear to be too small to be directly related to the acoustic wave scattering from boundaries. Our modified-Callaway requires boundary scattering lengths \(\gtrsim\) 30 nm to explain the current thermal conductivity measurements; interpreting the Raman FWHM as phonon confinement would predict boundaries spaced on \(~10\) nm scale, for the roughest wires.

An alternative possibility is that the broadening originates from crystal defects introduced by the etching process. While we know of no precedent for this with respect to the metal-assisted chemical etching, in previous studies, over-abundance of H\(_2\)O\(_2\) with respect to HF has been observed to generate porous Si away from the metal catalyst.\(^{[22]}\) Both our MacEtch solutions utilize a high ratio of HF:H\(_2\)O\(_2\) to avoid this and we do not observe discernable porosity by TEM. However, we believe it is possible that clusters of point defects, which would be difficult to detect by TEM, could form in the bulk of the nanowire. Disorder can relax the selection rules for Raman scattering, leading to spectrum broadening.\(^{[44]}\)
In summary, a technique for fabricating vertically aligned Si nanowires with controlled roughness based on a two-step wet etch process has been presented and used to study the thermal transport properties of rough Si nanowires with similar diameter and surface correlation length using time-domain thermoreflectance. The measured thermal conductivity of highly roughened nanowires are found to be significantly below the boundary scattering limit predicted based on a modified Callaway model and below that previously measured for smooth single nanowires of similar diameter. The lowest thermal conductivities are similar to that previously reported on individual roughened nanowire. However, in all nanowire arrays with low thermal conductivity, we observe significantly broadened Raman linewidths. The origin of the broadening is not well-understood, but could indicate microstructural changes that affect acoustic phonons.

Experimental

*Roughness characterization:* Roughness of the nanowires was determined by high-resolution transmission electron microscopy (HRTEM). A double-tilt holder was used to tilt the nanowire to [110] zone-axis enabling high resolution imaging of the Si/native-oxide boundary (<1nm resolution). Several atomic resolution images recorded along the length of a nanowire are stitched together to generate the roughness profile of the nanowire over a length of ~500 nm, with the boundary being taken as the outmost edge of the lattice fringes; the boundary profile was fit to a linear function, considered to be the mean surface and the rms roughness and correlation length was calculated with reference to the mean surface as described in the main text. This procedure was conducted for three nanowires from each array to obtain an average rms roughness for each sample.
**Area fraction characterization:** The areal fraction and size distribution of each nanowire array was measured by analysis of top view SEM using the software package ImageJ. To prepare images for analysis, the images were thresholded and nanowires that were visibly clumped were separately manually with a 1 pixel line, so that the size distribution statistics were more representative. The area fraction observed from SEM over-predicts the nanowire size when the nanowires are rough, therefore once the roughness is measured, the SEM area fraction is reduced by a factor \((D - \delta D)^2 / D^2\), where the diameter reduction is given by \(\delta D = 2\sqrt{2}\delta_{rms}\). For the roughest nanowires reported, this correction reduces the area fraction by \(\sim 15\%\).

**Time-Domain Thermoreflectance (TDTR):** The time evolution of surface temperature is measured through temperature-dependent changes in the reflectivity, i.e., the thermoreflectance. We analyze the ratio of in-phase, \(V_{in}(t)\) and out-of-phase \(V_{out}(t)\), variations in the intensity of the reflected probe beam at the modulation frequency, \(f\), of the pump beam as a function of delay time, \(t\), between pump and probe\(^{[26]}\). The wavelength of the mode-locked Ti:sapphire laser is \(\lambda = 785\) nm and the \(1/e^2\) radius of both focused beams is \(14\) µm. Pump and probe laser power were set to \(20\) mW and \(14\) mW respectively, which is calculated to produce \(<1K\) steady state temperature rise. Aluminum transducer thickness was measured using picosecond acoustics. Our TDTR approach has been thoroughly validated and extensively applied in studies of the thermal conductivity of thin films\(^{[31]}\) and the thermal conductance \(G\)^{[45]} of interfaces. Sources of error in the measurement total \(\sim 20\%\) in the current measurements and have been discussed in the main text.

**Raman scattering:** the Stokes shift in the backscattering geometry was collected using a 488 nm laser focused to a 5 µm \(1/e^2\) radius with 2 mW intensity. The signal was analyzed
using an Acton InSight spectrometer with 2.0 cm\(^{-1}\)/pixel bandwidth. We estimate that the laser power of 2 mW produces less than a 10 K steady state temperature rise in the lowest thermal conductivity samples; we verified that the Raman peakwidths and peak positions do not depend on laser intensity. The measured peakwidth of bulk Si in our system is 4.24 cm\(^{-1}\); treating the measured intensity as a Lorentzian convolved with Gaussian function that describes the instrumental broadening,\(^{[34]}\) using the bulk Si peakwidth of 2.6 cm\(^{-1}\),\(^{[34]}\) the FWHM of the instrumental broadening is \(~2.6\) cm\(^{-1}\).

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Figure 1. (A) Bright field transmission electron micrographs of nanowires obtained by post-roughening process (etch times increasing from left to right: 2, 10, 16 seconds respectively); the scale bar in the upper left corner of the left panel is 10 nm). Nanowires are aligned along the [110] zone axis. (B) rms roughness of Si nanowires after the post-roughening process, as determined from HRTEM images. Each point represents the average rms roughness for 3 wires from the same nanowire array.
Figure 2. (A) Effective thermal conductivity of several nanowire composite layers (open circles) measured as a function of the modulation frequency. The spin-on-glass (solid circles) displays no significant frequency dependence. The low frequency limit of the measurements is used in conjunction with equations 2 & 3 to determine the thermal conductivity of the nanowires. (B) Silicon nanowire thermal conductivity for arrays of varied rms roughness: rms < 1nm (open squares), 1nm < rms < 2nm (open triangles), 2nm < rms < 3nm (open diamond), 3nm < rms < 4nm (solid circles). The theoretical prediction based on a truncated Callaway model\cite{32} (solid line) and previous measurements of a single VLS-grown smooth nanowire\cite{4} (cross) and a single EE rough nanowire\cite{14} (open circle) are shown for comparison.
Figure 3. (A) Height difference distribution functions measured for three representative nanowire arrays. (B) Thermal conductivity versus correlation length, $\xi_c$; solid and open circles are for nanowire profiles taken as the Si-SiO$_2$ interface and Air-SiO$_2$ interface respectively. (C) Thermal conductivity versus rms roughness, $\sigma$. 
Figure 4. (A) Raman scattering intensity for a 3.5 nm rms roughness nanowire array (solid circles), a 1.0 nm rms roughness nanowire array (solid square), and bulk silicon (open circles); Solid lines are best fit curves to the model, and the adjacent numbers are the associated FWHM. The open squares and it’s fit are scaled by 0.25 to avoid visual overlap with the solid circles. (B) Raman FWHM plotted against the etching time of the roughening process. (C) the position of the Raman peak plotted against the Raman FWHM. (D) The thermal conductivity of each nanowire array plotted against the corresponding Raman FWHM.