Ultralow Thermal Conductivity of Single-Crystalline Porous Silicon Nanowires

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Porous materials provide a large surface-to-volume ratio, thereby providing a knob to alter fundamental properties in unprecedented ways. In thermal transport, porous nanomaterials can reduce thermal conductivity by not only enhancing phonon scattering from the boundaries of the pores and therefore decreasing the phonon mean free path, but also by reducing the phonon group velocity. Herein, a structure–property relationship is established by measuring the porosity and thermal conductivity of individual electrolessly etched single-crystalline silicon nanowires using a novel electron-beam heating technique. Such porous silicon nanowires exhibit extremely low diffusive thermal conductivity (as low as 0.33 W m\(^{-1}\) K\(^{-1}\) at 300 K for 43% porosity), even lower than that of amorphous silicon. The origin of such ultralow thermal conductivity is understood as a reduction in the phonon group velocity, experimentally verified by measuring the Young’s modulus, as well as the smallest structural size ever reported in crystalline silicon (<5 nm). Molecular dynamics simulations support the observation of a drastic reduction in thermal conductivity of silicon nanowires as a function of porosity. Such porous materials provide an intriguing platform to tune phonon transport, which can be useful in the design of functional materials toward electronics and nanoelectromechanical systems.

1. Introduction

The urgent need for utilizing tremendous waste heat and heat management has led to extensive studies on how to tune the thermal conductivity of materials, which have wide applications in thermoelectrics, thermal sensors, and other microsystems.[1–7] One way to reduce thermal conductivity is by creating ordered structures in thin films and bulk materials, called phononic crystals, which generate a bandgap by forbidding certain frequency phonons and redistributing the phonon density of states.[8–11] An alternative approach is that of nanostructuring to reduce structural dimensions to length scales that are comparable to or less than the phonon mean free path. The thermal conductivity of bulk silicon is 150 W m\(^{-1}\) K\(^{-1}\) (300 K), while silicon nanowires with enhanced point defects, reduced diameter, and rough surfaces can exhibit up to 100-fold reduction in thermal conductivity.[3–6] Porous materials can affect phonon transport by decreasing structure size and accordingly reducing the effective phonon mean free path.[12] A higher porosity with small structure size is expected to lead to lower thermal conductivity due to phonon confinement effects,[13] arising from a reduced number of phonon channels as well as due to enhanced scattering of phonons at the pore interface.[14]
Pore-like structures in materials could also produce non-propagating phonon modes and lower the phonon group velocity.\[15,16\] Experimentally, thermal conductivity as low as 1.68 W m\(^{-1}\) K\(^{-1}\) at room temperature was reported by Zhang et al.\[17\] through the fabrication of vertically aligned porous silicon arrays, albeit with unknown porosity. In addition, employing the crude kinetic theory expression,\[18\] \(\kappa = \frac{1}{3} Cv_l\), where \(C\) is the volumetric heat capacity, \(v\) is the average phonon group velocity, and \(l\) is the phonon mean free path, the thermal conductivity can be seen to scale with the phonon group velocity, which is equal to the speed of sound, \(v_s\), in the low frequency limit. It has been predicted that a porosity of 30% results in a reduction in the Young’s modulus, \(E\), of porous silicon by half, which also leads to impeded phonon transport since \(\kappa \sim \rho v_s E\), where \(\rho\) is the mass density.\[19,20\] Although simulations have predicted such phonon transport behavior in porous structures, there are still no structure–property relations that account for porosity and quantify its effects on thermal conductivity. Gravimetric\[21\] and gas adsorption measurements\[17\] are useful in obtaining the average porosity across bulk porous samples, but such techniques cannot be adopted for single-porous nanostructures like nanowires, nanotubes, or thin films. The classical Eucken\[22\] and Russel models\[23\] are usually employed to predict thermal conductivity for bulk porous materials with periodically aligned cylindrical pores, or phononic crystals. The models assume a uniform arrangement of solid cubes and individual pores and then calculate the effect of porosity on the bulk thermal conductivity, but neglect the effect of nanoscale structure size and possible phonon-interface scattering. Therefore, not only is an accurate measurement of nanoscale porosity important, but understanding the effect of pores while accounting for structure size scattering of phonons is a key necessity.

In this work, we measure the porosity and thermal conductivity of individual silicon nanowires by employing an electron-beam technique.\[24\] We show that the actual cross-sectional area of the nanowire is directly proportional to the absorbed electron-beam energy. We also employ high-resolution transmission electron microscopy (HRTEM) to quantify the average structure size in individual porous nanowires, and to confirm their continuously single-crystalline backbone. Then, we use an effective diffusive thermal transport model to explain the dependence of the thermal conductivity on the nanostructure size, while considering the expected change in group velocity as well as a reduced mean free path. We show experimentally that the Young’s modulus of these porous silicon nanowires is smaller compared with to bulk silicon, which translates to an expected decrease in the phonon group velocity. We also employ molecular dynamics simulations to validate the observed dependence of thermal conductivity on the porosity of these silicon nanowires. These porous silicon nanowires with ultralow thermal conductivity may find new applications as thermoelectric (TE) materials.

2. Results and Discussion

Porous silicon nanowires were fabricated by metal assisted chemical etching,\[25–27\] as detailed in Section S1 of the Supporting Information. Figure 1a shows the as-grown porous silicon nanowires on the substrate. To make sure that the porous silicon nanowires were indeed continuously single-crystalline, TEM diffraction pattern with a selected area diffraction
The formula shows that the thermal conductivity, \( \kappa \), of the porous silicon nanowire is given by

\[
\kappa = \frac{1}{\frac{dR}{dx} \cdot A}
\]

In order to accurately determine the thermal conductivity, we need to obtain the actual cross-sectional area, \( A \), of the porous silicon nanowire, which is defined as the solid, nonporous silicon nanowire. The actual cross-sectional area is calculated using the CASINO Monte Carlo program, as for a fixed electron beam energy, \( E \), the loss of the incident electron energy scales with the cross-sectional area of the nanowires. By using the CASINO Monte Carlo program, we find that for a fixed electron beam energy, \( E \), the loss of the incident electron energy scales with the cross-sectional area of the nanowires. Consequently, as the focused electron beam is raster scanned across the nanowire cross-section, we can deduce the dimension of an unknown specimen if its absorbed energy is measured. By using the CASINO Monte Carlo program, we find that for a fixed electron beam energy, \( E \), the loss of the incident electron energy scales with the cross-sectional area of the nanowires. To experimentally verify the validity of this absorption power law, solid silicon nanowires with different diameters were placed on the same METS device as that used for the porous silicon nanowire thermal conductivity measurement. Following this, thermal contact was made using EBID to each nanowire, in a manner similar to that for the already suspended porous silicon nanowire. HRTEM imaging and diffraction were carried out as well for the solid silicon nanowires prior to manipulation (Figure S5, Supporting Information). An electron beam with energy of 18 keV was then scanned across each solid silicon nanowire and finally across the porous silicon nanowire. The temperature rise at both left and right islands was recorded. Four such devices with calibrated thermal resistance of the platinum beams were tested and the absorbed power was plotted as a function of cross-sectional area of the solid nanowires (\( A = \pi d^2 / 4 \), where \( d \) is the diameter of each solid nanowire) as shown in Figure 3b. The linear relation between the absorption power and the cross-section area of the nanowires is seen.
for the solid silicon nanowires on different METS devices in Figure 3b, corroborating the CASINO simulation results.

In order to then calculate the actual (i.e., solid) cross-sectional area of the porous silicon nanowire, the experimentally measured absorption power is obtained from the slope, as shown by the black star in Figure 3b. The apparent cross-sectional area for the porous silicon was obtained by tilting the SEM stage by 90° and imaging the cross-section, as discussed in Figure S2 (Supporting Information). Therefore, porosity for the porous silicon nanowire is calculated as

$$P = 1 - \frac{S_{\text{actual}}}{S_{\text{apparent}}}.$$ 

The SEM image for this setup is shown in Figure 3c and the one-to-one comparison of thermal conductivity and porosity, each measured on the same porous nanowire, is summarized in Figure 3d. Note that for the calculation of the thermal conductivity, the actual cross-sectional area determined as described above is used, not the apparent area as visible from the SEM.

In order to understand the abnormally low thermal conductivity of porous silicon nanowires and its dependence on porosity, we employ a modified phonon radiative heat transfer (EPRT) model pioneered by Majumdar,\textsuperscript{[29]} where phonons are considered as energy packets moving ballistically within the crystalline part of the nanowire until scattered diffusively by the surface at the pore. In this model, the phonon mean free path is considered to be frequency independent, called the gray-body approximation. This is important in our case of porous nanowires, since we expect that interface scattering at the pores must be the dominant scattering factor that reduces the thermal conductivity. Here a single average phonon acoustic branch (accounting for two transverse and one longitudinal branches) was considered as has been used both theoretically\textsuperscript{[30,31]} and experimentally\textsuperscript{[12]} for phonon transport in porous structures with relatively small errors. This effective EPRT model provides an informative general expression for the thermal conductivity in porous materials whereby we can account for the pore morphology through the structure size, defined as $d$.

The size-dependent thermal conductivity can then be written as

$$\kappa(T, d) = \frac{1}{3} C(T) v \left( \frac{1}{\tau_{\text{bulk}}(T)} + \frac{4}{3d} \right)^{-1},$$

where $\kappa(T, d)$ is effective thermal conductivity, $C(T)$ is the volumetric heat capacity, $v$ is the average phonon group velocity, $\tau_{\text{bulk}}(T)$ is the bulk phonon mean free path, and $d$ is the structure size of measured samples. $C(T)$ and $v$ are taken from Chen,\textsuperscript{[32]} by considering each acoustic-phonon polarization and excluding all optical phonons. The factor of $\frac{1}{3}$ that multiplies the structure size, $d$, is a correction on the traditional Fourier’s law, arising from solving the phonon radiative heat transfer equation and is particularly relevant in our case as $d << L$, where $L$ is the length of the nanowire. The temperature-dependent bulk phonon mean free path, $\tau_{\text{bulk}}(T)$, is calculated by using $C(T)$ and $v$ together with the thermal conductivity of bulk silicon.\textsuperscript{[13]} For porous silicon nanowires, the average crystalline size is obtained by measuring the surface periodicity of pores in HRTEM, details about which are provided in the Supporting Information. Our measured
structure size is 4.3 (±1.5) nm, smaller than that reported by Gesele et al.[34] and Sui et al. [35] Interestingly, the structure size does not seem to depend on the porosity, indicating that for larger-porosity samples, the pore sizes are larger for the same apparent cross-sectional area of the nanowire. This fit is shown as a dotted line in Figure 4a, in comparison to our data on single nanowires as well as some other experimental results on porous silicon and holey silicon thin film,[8,36–38] down to a structure size of few nanometers. It is clear that the EPRT model overestimates the thermal conductivity for all the porous silicon samples, irrespective of the sample fabrication technique. We hypothesize that for porous structures the Young's modulus is reduced considering the high surface-to-volume ratio, thus reducing the phonon group velocity.[20] To prove this, we measured the Young's modulus of our porous silicon nanowires by the commonly employed three-point bending method[39,40] and the measurement results are shown in Figure 4c, with details summarized in the Supporting Information. The Young's modulus of both high and low porosity silicon nanowires is a few times smaller than that of both solid silicon[41,42] and SiO 2.[43] The resulting effective group velocity can then be written as $v_{\text{eff}} = \frac{E_{\text{porous}}}{E_{\text{solid}}} \times v$, where $E_{\text{porous}}$ and $E_{\text{solid}}$ are the measured Young's modulus for the porous and solid silicon nanowires and $v$ is the group velocity of bulk silicon. We obtain a correction to the experimental thermal conductivity due to this effective value of phonon velocity, $\kappa_{\text{eff}} = \kappa_{\text{measured}} \times \frac{v_{\text{eff}}}{v}$.

We also estimate a similar effective phonon group velocity for other porous structures shown in Figure 4a, based on $v_{\text{eff}} = (1 - P) \times v$, where $P$ is the porosity (for literature data) porosity; the final effective thermal conductivity is shown as black open circles in Figure 4a (a summary of these results is tabulated in Table S1 in the Supporting Information). This elegant result shows that over a large range of structure sizes, ranging from ≈5 nm (our data) up to ≈500 nm, the EPRT model captures the scaling of the effective thermal conductivity as a function of structure size very well and especially for our highly porous silicon nanowires. The accuracy of such a calculation can be improved further by considering frequency-dependent boundary scattering of the phonons. Note here also that the bulk silicon specific heat is employed for the single-crystalline porous silicon nanowires in the temperature range of our measurement, following the treatment of previous work,[20] and a further discussion about the feasibility of this assumption can be found in the Supporting Information.

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**Figure 4.** a) Thermal conductivity dependence on the structure size at 300 K (color version online). The black line is the extracted effective conductivity derived from the thermal phonon radiative transport (EPRT) model from Majumdar. For comparison, holey silicon[37] (Tang et al.), porous silicon[36] (Lysenko et al.), and phononic nanomeshes[8,38] (Kim et al. and Yu et al.) with different structure sizes are plotted. The effective fitting is obtained by considering porosity-induced effective phonon velocity to obtain the effective thermal conductivity, $\kappa_{\text{eff}}$, and compared to the Majumdar model, as described in the text. b) Thermal conductivity plotted as a function of $(1 - P)$, where $P$ is the porosity of the silicon nanowires. Here, we expect that the effective phonon group velocity, $v_{\text{effective}}$, is proportional to $(1 - P)$. c) The Young's modulus of our measured porous silicon nanowires, compared with crystalline silicon nanotubes (c-Si NTs)[20] and crystalline silicon nanowires (c-Si NWs).[31] To test the measurement accuracy, we measure the Young's modulus of solid silicon nanowires with different diameters (blue solid squares) and amorphous SiO 2 nanowires (green solid diamonds), which is comparable to that of bulk silicon[41,42] and bulk SiO 2.[43] d) Temperature-dependent thermal conductivity of porous silicon nanowire with porosity of 34.48% (red circles) and 42.78% (black squares) together with a-Si (green triangles) and a-Si:H (purple diamonds).[46] On the right side is the temperature-dependent specific heat for bulk silicon. The black solid lines are fitted from the EPRT model.
To investigate the critical effect of phonon softening that manifests as a reduced group velocity we replot the measured thermal conductivity as a function of \((1-P)\), where \(P\) is the porosity of each silicon nanowire in Figure 4b, where \(\tau_{\text{eff}}\) is proportional to \((1-P)\), deduced from the reduction in the Young’s modulus as explained above, and the linear trend is very clearly observed. For different porosity silicon nanowires with similar structure size, the effective phonon group velocity therefore proves to be the dominant factor that tunes thermal transport. It has been shown theoretically that for nanostructured silicon samples, the group velocity of broadband phonon modes that carry heat is softened greatly as well\(^{[37]}\) and a further discussion about the porous silicon nanowires is shown in Section S8 in the Supporting Information.

In addition, temperature-dependent thermal conductivity of two porous silicon nanowires was investigated by the traditional thermal bridge method.\(^{[4,46]}\) As shown in Figure 4d, the thermal conductivity of the single porous silicon nanowires is nearly insensitive to temperature in the temperature range from \(\approx 120\) to 300 K and decreases with temperature below \(\approx 120\) K, following a trend that is expected from the \(C(T)\).\(^{[15]}\) Unlike amorphous silicon,\(^{[46]}\) which implies that indeed the limited structural size plays the dominant role in impeding phonon transport. For these nanoporous systems, phonons with low frequency (long wavelength) have a large mean free path and are the dominant thermal carriers.\(^{[49]}\) These phonons are expected to scatter mainly from the porous boundaries and preserve the independence of thermal conductance from temperature, as inelastic phonon-phonon scattering is expected to be weaker. This is also reflected in the EPRT model, shown as the black line\(^{[29]}\) in Figure 4d, and suggests that the local temperature equilibrium in the nanocrystallite structure along the nanowire is maintained by thermalizing and diffusive boundary scattering. The low temperature decrease in thermal conductivity is consistent with a concomitant reduction in the specific heat.

In porous silicon nanowires with a crystalline skeleton size as small as \(\approx 5\) nm, it is difficult to avoid partial oxidation on the surface of the crystalline backbone, as the native oxide layer for crystalline silicon is expected to be \(\approx 1-2\) nm. Since these nanowires show ultralow thermal conductivity, a convincing verification to ensure that the nanowire is continuously crystalline is the measurement of electrical conductivity. Hence, four probe electrical conductivity measurements were conducted on the METS device. For a freshly fabricated porous silicon nanowire, electrical resistivity of 9.6 \(\Omega\) m was observed, which is five orders of magnitude larger compared to the resistivity of the silicon wafer used to etch the nanowires \(\approx 5.0 \times 10^{-5}\) \(\Omega\) m, similar to other reports in the literature.\(^{[5,17]}\) In order to improve the electrical conductivity, an aluminum (Al) thin film was employed as a doping source (details of the doping are discussed in Section S4 of the Supporting Information) since Al has been shown to be an effective acceptor for silicon doping.\(^{[50]}\) The electrical resistivity of Al-doped porous silicon nanowires was measured as 5.9 \(\times 10^{-2}\) \(\Omega\) m while the thermal conductivity of the same nanowire was measured to be 0.48 W m\(^{-1}\) K\(^{-1}\) at 300 K. Therefore, a reduction by about \(\approx 160\%\) in the electrical resistivity with a negligible change in the thermal conductivity was observed for Al-doped porous silicon nanowires. A possible application for electrically conductive, low thermal conductivity materials is in thermoelectrics, but the electrical conductivity needs to be increased by a further three to four orders of magnitude in order to maximize the thermoelectric power factor, while maintaining low thermal conductivity. Postdoping,\(^{[5,51]}\) like Boron and Gallium ion implantation, can be carried out to improve the electrical conductivity further, but is beyond the scope of our current work.

Given the large surface-to-volume ratio, the morphology at the pore surface can also change the nature of scattering and hence the thermal conductivity. In order to minimize the surface energy, the free bonds at the pore surface are usually passivated by oxygen or hydrogen.\(^{[52]}\) This passivation of atoms leads to further energy exchange between the silicon atoms by changing their vibrational spectra.\(^{[47]}\) For porous silicon nanowires, surface oxygen passivation during electrochemical etching cannot be avoided, and can develop when exposed to atmosphere or moisture even for a few minutes. This could be a source for additional anharmonic scattering due to softening of surface phonon modes and serves as an alternative possible mechanism to explain the low thermal conductivity of the porous silicon nanowires, together with the dominant phonon-boundary scattering. Indeed, the formation of Si–O bonds at the surface of the nanowires is observed via Raman scattering, confirming the presence of such surface passivation in our porous silicon nanowires (Section S5, Supporting Information).

In order to understand better the effect of porosity on thermal transport, nonequilibrium molecular dynamics (NEMD) was employed by using LAMMPS software.\(^{[53,54]}\) The simulation details are discussed in the Supporting Information and an illustrative geometry with thermal conductivity extraction is detailed in Figure 5a. Increasing porosity leads to more phonon-interface scattering, which decreases the thermal conductivity sharply. Figure 5b shows the thermal conductivity dependence on the porosity for porous silicon nanowires and the inset is a silicon nanowire with porosity of 43.6%. The normalized thermal conductivity (with respect to the thermal conductivity of a crystalline silicon nanowire of the same diameter) as a function of porosity is shown in the inset of Figure 5b. The thermal conductivity of the porous silicon nanowire with a porosity of 43% is decreased by one order of magnitude compared to that of a solid silicon nanowire due to the scattering by pores. A reduction in thermal conductivity by a factor of \(\approx 3\) is observed when the porosity is increased from 22% to 43%, which is in line with our experimental observation at 300 K, with the thermal conductivity reduced by a factor of \(\approx 4\) for a porosity increase from 25% to 40%. Similar to the experimental observation of a reduced Young’s modulus in porous silicon nanowires, we expect a softening effect in the simulations too.\(^{[55]}\) The Young’s modulus of the same porous silicon structure can be obtained by NEMD with the simulation details shown in Figures S11 and S7 (Supporting Information). Here, the Young’s modulus is shown to decrease strongly as the porosity increases, leading to a concomitant decrease in the phonon group velocity. In correspondence with the experimental conditions, the oxygen passivation effect is investigated as well, which
decreases the Young's modulus further for the same porosity. Note here that a direct comparison with \((1 - P)\) similar to the experiments is not possible since the pore distribution in the NEMD structures is not homogeneous, unlike in our porous nanowires.

3. Conclusion

In conclusion, single-crystalline porous silicon nanowires have been fabricated to study the effect of porosity on thermal transport. By means of electron-beam-based power absorption measurements on single nanowires, their porosity is experimentally obtained and the thermal conductivity is measured on the same nanowires. The small structure size \((\approx 5 \text{ nm})\), as well as the softening effect due to reduced Young's modulus of porous silicon nanowires, impedes phonon diffusive transport, giving a thermal conductivity as low as 0.33 \(\text{W m}^{-1} \text{K}^{-1}\) at 300 \(\text{K}\) while maintaining modest electrical conductivity after Al-doping. Our study shows that by enhancing phonon-surface scattering in nanostructures with a large surface-to-volume ratio, it is possible to tune thermal conductivity in single-crystalline materials below their amorphous analogs, which is not only interesting fundamentally, but can also be very useful in applications such as insolation barriers for thermal management applications and in thermoelectrics. Mapping the internal structure of such homogeneously porous nanowires to thermal conductivity will be of both theoretical and experimental interest for future studies.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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electron-beam technique, molecular dynamics, porous silicon nanowires, thermal conductivity, Young's modulus

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