Lattice thermal conductivity of nanoporous Si: Molecular dynamics study

J.-H. Lee and J. C. Grossman
Berkeley Nanosciences and Nanoengineering Institute, University of California-Berkeley, Berkeley, California 94720, USA

J. Reed
Lawrence Livermore National Laboratory, Livermore, California 94550, USA

G. Galli
Department of Chemistry, University of California-Davis, Davis, California 95616, USA

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Lattice thermal conductivity \( \kappa_l \) of Si with nanometer-sized pores along the [001] direction is calculated as a function of pore diameter \( (d_p) \) and pore spacing \( (d_s) \) by employing a molecular dynamics approach. Our results show that \( \kappa_l \) across pores is smaller than the bulk value by over two orders of magnitude at room temperature, and that it decreases (increases) as a function of \( d_p \) \( (d_s) \) for fixed \( d_s \) \( (d_p) \). This behavior is shown to originate from the reduction in the channels for phonon transport and the increased phonon scattering at the pore surfaces. © 2007 American Institute of Physics. [DOI: 10.1063/1.2817739]

Improvements in thermoelectric (TE) materials could lead to efficient solid state energy conversion for environmentally benign power generation and refrigeration. This realization would require a dramatic increase to \( \sim 3^1 \) in the thermoelectric figure of merit \( ZT=S^2\sigma T/\kappa \) (\( S \) is the Seebeck coefficient, \( \sigma \) the electrical conductivity, \( T \) the absolute temperature, and \( \kappa \) the total thermal conductivity, respectively) by which the efficiency of TE materials is described. Experimentally, however, the ZT of TE materials has been only marginally increased from about 0.6 to 1 over the past several decades due to the challenge in simultaneously optimizing \( S \), \( \sigma \), and \( \kappa \), as these quantities are interdependent.1

Theoretical predictions made by Hicks and Dresselhaus in the early 1990s2 showed that ZT could be greatly increased for TE materials in their reduced dimensionality such as superlattices (SLs) and quantum wires. Recent experiments verified these predictions for room-temperature \( \text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3 \) SLs3 and \( \text{PbSeTe/PbTe} \) quantum dot SLs,4 yielding ZT of 2.4 and 1.3–1.6, respectively, which makes these materials appealing for cooling devices. The enhancement in ZT in these superlattices is believed to originate from the reduction of the lattice thermal conductivity \( (\kappa_l) \) arising from phonon boundary scattering as opposed to an improvement in the electronic properties.5

There have also been attempts to increase ZT using bulk TE materials, which include complex structures such as skutterudites, clathrates, half-Heusler alloys, and chalcogenides.6 These attempts are all focused on reducing \( \kappa_l \) because it is the dominant contribution to \( \kappa \) in semiconductors. Bulk TE materials yield moderately high ZT values \( (~1) \) at elevated temperatures due to the reduced \( \kappa_l \) and may be useful for power generating applications. The reduction of \( \kappa_l \) in these systems is due to either the introduction of “rattling” atoms that cause phonon scattering in cage structures such as skutterudites or to the effect of disorder induced by differences of mass and atomic sizes in half-Heusler alloys.

Instead of using complex materials, there have been recent attempts to use Si for TE applications due to its structural simplicity and the possibility of utilizing existing Si-based manufacturing processes. Some of the most studied silicon structures for TE applications are based on Si nanowires.7–9 While these materials show promise, the measured thermal conductivities are still too high for practical applications, which require \( \kappa \leq 2 \text{ W/mK} \).5 e.g., measurements yield \( \kappa \sim 7 \text{ W/mK} \) at 300 K, whereas a recent Monte Carlo study gives \( \kappa \sim 12 \text{ W/mK} \) for 22 nm diameter nanowires. Since, however, both experimental and theoretical studies seem to indicate that the thermal conductivity is decreased as the nanowire diameter is decreased, lower \( \kappa \) may be expected for nanowires with smaller diameter. Interestingly, recent molecular dynamics (MD) studies found that at very small diameter (<1.5 nm), the thermal conductivity increases,9 suggesting a range of diameter of Si nanowires for TE applications. Surface modification may also lead to further decrease of \( \kappa \).

Another structure of interest is the Si clathrate in which tetrahedrally bonded Si atoms form a framework of cages that can accommodate large metal atoms.10 While Type I \( (\text{Si}_{196}) \) and Type II \( (\text{Si}_{136}) \) clathrates are being considered, attempts to optimize the TE properties in these structures have only recently begun: recent MD simulations on the Type II Si clathrate lead to a reduction in the thermal conductivity of a factor of 5–8 compared with that of bulk Si,11 which implies that much work remains to be done along this direction.

Several experiments12,13 also stimulated large interest in porous Si for possible TE applications: the room-temperature thermal conductivity of this material can be as low as 0.1 \text{ W/mK} when the volume fraction of pores (i.e., porosity) becomes 0.64–0.89.12 While this value is extremely low, the randomness of the pore shapes and arrangement makes theoretical studies difficult14 and appears to deteriorate substantially the electronic properties.15

Recently, the in-plane \( \kappa_t \) of Si films with circular micrometer-sized pores (microporous Si) was observed to be significantly lower than bulk Si at room temperature14 and subsequent theoretical studies based on a Boltzmann transport equation approach with two-dimensional nanocompos-

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Electronic mail: jhyoung73@berkeley.edu.
ites verified the experimental observation.\textsuperscript{15,16} As mentioned previously, however, the observed $\kappa_i$ is found to be still too large ($\sim 40$ W/mK) for applications.

In the present work, a classical MD approach is used to calculate the transverse thermal conductivity of Si with periodically arranged \textit{nanometer-sized} cylindrical pores along the [001] direction at room temperature. Here, the transverse conductivity $\kappa_\perp$ is defined as the thermal conductivity in the plane perpendicular to the pore axis. Our calculations show that: (i) $\kappa_i$ of this nanoporous Si is reduced by more than two orders of magnitude compared to the bulk as the porosity increases, and (ii) the thermal conductivity becomes smaller for small pores at a given porosity due to a decrease of the phonon mean-free path which arises from increased phonon scattering at the pore surfaces. In addition, the contribution from the ballistic character of the phonon transport\textsuperscript{16} in determining $\kappa_\perp$ is found to be important for small porosity only ($\leq 0.2$). These findings make nanoporous Si an attractive candidate for TE cooling applications.

The structure of nanoporous Si used in our calculations is shown in Fig. 1. Pores are along the [001] direction and passivated with H atoms on the surface. In order to examine the dependence of $\kappa_\perp$ on the pore diameter ($d_p$) and the pore spacing ($d_s$), separately, we consider two distinct cases: (1) $d_p$ is fixed at 1.0 nm while $d_s$ is varied and (2) $d_s$ is fixed at 1.0 nm while $d_p$ is varied. Specific values of $d_p$ and $d_s$ used for each case are listed in Table I.

All MD simulations were performed at 300 K for 2 ns with a time step $\Delta t=0.02$ fs, and a Tersoff potential\textsuperscript{17} was used to describe the interatomic potential. Periodic boundary conditions and a microcanonical ensemble are employed for the simulations. $\kappa_\perp$ was calculated from the Einstein relation,\textsuperscript{18} which for a $N$-particle system is

$$\kappa_\alpha = \frac{1}{V k_B T} \lim_{t \to \infty} \frac{1}{2t} \langle [R_\alpha(t) - R_\alpha(0)]^2 \rangle$$

with

\begin{equation}
R_\alpha = \sum_i r_{i\alpha} \left( \frac{p_i^2}{2m_i} + \frac{1}{2} \sum_j u_{ij} \right),
\end{equation}

where $r$, $m$, and $p_i$ are the position, mass, and momentum of the $i$th particle, respectively, $\alpha$ is a cartesian component, $V$ is the simulation volume, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, and $u_{ij}$ is the potential energy between the $i$th and $j$th particles. For a given simulation, $\kappa_i$ and $\kappa_s$ are averaged due to the planar symmetry to obtain $\kappa_\perp$ and for each variation of ($d_p, d_s$), an ensemble average is taken from five separate MD simulations with different initial conditions.

We note that the use of periodic boundary conditions makes it important to test convergence of $\kappa_i$ with respect to the simulation cell size\textsuperscript{19} which was done by evaluating $\kappa_\perp$ at $d_p=1.0$ nm as a function of both the number of periodically repeating simulation cells along the pore axis and the number of pores within an in-plane unit cell. These test calculations show that $\kappa_\perp$ is fairly insensitive to the number of axial repeat units and well-converged with three unit cells along the pore axis; $\kappa_\perp$ is also converged with respect to in-plane repeat units with a single unit cell, assuming that much longer-range phonon modes ($>5$ nm) are absent, a premise consistent with any realistic material containing defects. We note that the use of the Boltzmann statistics in our simulations is an approximation leading to underestimated values of $\kappa_\perp$, possibly by 20%–30% (see, e.g., Ref. 20).

The calculated $\kappa_i$ is presented in Fig. 2 as a function of $d_s$ ($d_p$) for fixed $d_p$ ($d_s$). Clearly, $\kappa_\perp$ increases as $d_s$ increases when $d_p$ is fixed, while $\kappa_\perp$ decreases when $d_p$ increases with $d_s$ fixed. This is easily understood by considering porosity ($\phi$), defined as $\phi = \pi d_p^2/(2(d_p+d_s))^2$ and listed in Table I; increased pore volume reduces the channels for phonon transport, hence leading to a decrease in $\kappa_\perp$.

However, while $\kappa_\perp$ generally decreases as $\phi$ increases, Fig. 2 shows that in some cases, $\kappa_\perp$ can be small even for small values of $\phi$. To illustrate this more clearly, three of the points in Fig. 2 have been labeled as $p1$, $p2$, and $p3$. Note that $\kappa_\perp$ at $p1$ is smaller by 40% than that of $p2$ and $p3$ in Fig. 2 even though $\phi$ is smaller at $p1$. This can be explained by taking into account the surface-to-volume ratio ($\rho$), defined as $\rho = \pi d_p^3/(d_p+d_s)^2$ which correlates with the phonon scattering at the pore surface. Table I shows that $p1$ has over 60% higher $\rho$ than $p2$ and $p3$ even though $\phi$ at $p1$ is about 6% and 21% lower than that of $p2$ and $p3$, respectively. This implies, depending on $\phi$ and $\rho$, that the phonon scattering at
the pore surface can be more important in determining the thermal conductivity of nanoporous Si than the increase in the number of transport channels.

Our calculations show that \( \kappa_{\perp} \) of nanoporous Si is significantly lower than that of pure bulk Si, which is calculated to be 273±18 W/mK at 300 K using the same simulation approach. This value represents an overestimate of the experimental value (by about 80%), due to the tendency of the Tersoff potential to yield Si bonds that are too stiff. However, the trend found here is significant and we believe that the use of the Tersoff potential gives a correct qualitative picture of heat transport in Si based materials. In our calculations, the largest \( \kappa_{\perp} \) is 7.1±1.5 W/mK for \((d_p, d_s) = (1.0, 2.26 \text{ nm})\), almost 40 times lower than the bulk value and even smaller than that of microporous Si by a factor of 6. Furthermore, one can easily see from Table I and Fig. 2 that with moderate porosity \((d_s \geq 0.2)\), \( \kappa_{\perp} \) for the fixed \( d_p \) cases becomes almost 300 times smaller \((\leq 1 \text{ W/mK})\) than the bulk value, which could make nanoporous Si highly attractive for TE cooling applications.

The thermal conductivities of porous Si were theoretically modeled in Ref. 16 by taking into account the ballistic character of phonon transport, which becomes important when the pore spacing is comparable to the phonon mean-free path. Following the same approach, we plot in Fig. 3(a) the calculated \( \kappa_{\perp} \) values along with a fitting function \( \kappa_{\beta} \), which is defined as

\[
\kappa_{\beta}(d_p, \phi) = \kappa_0 \frac{d_p}{d_p + A \sqrt{\phi / F(\phi)}},
\]

where \( \kappa_0 \) is the thermal conductivity of bulk Si, \( F(\phi) = \sqrt{4 \phi / \pi (\sin^{-1}(\sqrt{\phi / \pi} - \pi / 2) + \sqrt{1 - 4 \phi / \pi})} \), and the fitting parameters are \( A = 50.9, B = 1821.1, \) and \( \gamma = 1.9 \), respectively. In Eq. (3), the ballistic character of phonon transport is described by \( F(\phi) \) as discussed in Ref. 16, whereas \( f(\phi) \) accounts for the phonon diffusion. It is clear from Fig. 3(a) that the calculated \( \kappa_{\perp} \) is well-fitted with \( \kappa_{\beta} \). It is to be noted that \( \kappa_{\perp} \) for \( d_p \leq 0.4 \text{ nm} \) does not correspond to a realistic material because \( d_s \approx 0.4 \text{ nm} \) corresponds to removing a single Si chain along the [001] direction.

As is clear from Fig. 3(a), \( \kappa_{\perp} \) decreases as \( d_p \) decreases at a given porosity, reflecting the increased phonon scattering at the pore surface, as mentioned earlier. Furthermore, the decrease in \( \kappa_{\perp} \) is more pronounced when \( \phi \) is small \((\leq 0.2)\), which can be understood by introducing another fitting function \( f(\phi) = \kappa_0 f(\phi) \), the same function as in Eq. (3) with \( A = 0 \). It is to be noted that the \( d_p \)-dependence of \( \kappa_{\perp} \) is lost in \( \kappa_{\beta} \), which implies that it is the ballistic character of phonon transport that makes \( \kappa_{\perp} \) dependent on \( d_p \). In Fig. 3(b), we present the difference between \( \kappa_{\beta} \) and \( \kappa_{\perp} \). From Fig. 3(b), we see that the dependence of \( \kappa_{\perp} \) on \( d_p \) (thus, on the ballistic phonon transport) is larger for smaller \( \phi \) and becomes negligible when \( \phi \) increases, which is due to the fact that phonon mean-free paths decrease for the reduced transport channels.

In summary, in the present work, a series of classical MD simulations were performed to calculate the transverse thermal conductivities of nanoporous Si with a view to TE applications. The obtained conductivities range from 7.1 to 0.6 W/mK which is smaller by over two orders of magnitude than that of bulk Si due to the reduction in the channels for phonon transport and the increased phonon scattering at the pore surfaces. In addition, the ballistic character of phonon transport in determining \( \kappa_{\perp} \) is found to be important only for small porosity. We note also that the present nanoporous Si may be more advantageous for electronic transport, which is important to achieve high ZT, due to periodic arrangement of pores as opposed to random porous systems, even though the latter show lower lattice thermal conductivity.

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\[1\] A. Majumdar, Science 303, 777 (2004).
\[6\] For a brief review, see, for example, K. Koumoto, I. Terasaki, and R. Funahashi, MRS Bull. 31, 206 (2006).