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Project Title:

First Principles Modeling of Phonon Heat Conduction in Nanoscale Crystalline Structures

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Abstract

The inability to remove heat efficiently is currently one of the stumbling blocks toward further miniaturization and advancement of electronic, optoelectronic, and micro-electro-mechanical devices. In order to formulate better heat removal strategies and designs, it is first necessary to understand the fundamental mechanisms of heat transport in semiconductor thin films. Modeling techniques, based on first principles, can play the crucial role of filling gaps in our understanding by revealing information that experiments are incapable of.

Heat conduction in crystalline semiconductor films occurs by lattice vibrations that result in the propagation of quanta of energy called phonons. If the mean free path of the traveling phonons is larger than the film thickness, thermodynamic equilibrium ceases to exist, and thus, the Fourier law of heat conduction is invalid. In this scenario, bulk thermal conductivity values, which are experimentally determined by inversion of the Fourier law itself, cannot be used for analysis.

The Boltzmann Transport Equation (BTE) is a powerful tool to treat non-equilibrium heat transport in thin films. The BTE describes the evolution of the number density (or energy) distribution for phonons as a result of transport (or drift) and inter-phonon collisions. Drift causes the phonon energy distribution to deviate from equilibrium, while collisions tend to restore equilibrium. Prior to solution of the BTE, it is necessary to compute the lifetimes (or scattering rates) for phonons of all wave-vector and polarization. The lifetime of a phonon is the net result of its collisions with other phonons, which in turn is governed by the conservation of energy and momentum during the underlying collision processes.

This research project contributed to the state-of-the-art in two ways: (1) by developing and demonstrating a calibration-free simple methodology to compute intrinsic phonon scattering (Normal and Umklapp processes) time scales with the inclusion of optical phonons, and (2) by developing a suite of numerical algorithms for solution of the BTE for phonons. The suite of numerical algorithms includes Monte Carlo techniques and deterministic techniques based on the Discrete Ordinates Method and the Ballistic-Diffusive approximation of the BTE. These methods were applied to calculation of thermal conductivity of silicon thin films, and to simulate heat conduction in multi-dimensional structures. In addition, thermal transport in silicon nanowires was investigated using two different first principles methods. One was to apply the Green-Kubo formulation to an equilibrium system. The other was to use Non-Equilibrium Molecular Dynamics (NEMD). Results of MD simulations showed that the nanowire cross-sectional shape and size significantly affects the thermal conductivity, as has been found experimentally.

In summary, the project clarified the role of various phonon modes—in particular, optical phonons—in non-equilibrium transport in silicon. It laid the foundation for the solution of the BTE in complex three-dimensional structures using deterministic techniques, paving the way for the development of robust numerical tools that could be coupled to existing device simulation tools to enable coupled electro-thermal modeling of practical electronic/optoelectronic devices. Finally, it shed light on why the thermal conductivity of silicon nanowires is so sensitive to its cross-sectional shape.

Summary of Research Accomplishments

Calculation of Phonon Scattering Time Scales

An approach based on the perturbation theory developed by Han and Klemens [1] was used to compute phonon scattering time-scales for all phonon modes, including optical phonons. Details of this approach may be obtained from the paper published as a result of this work [2]. Figure 1 shows computed scattering time-scales using the method developed in this study, along with comparisons with published results.

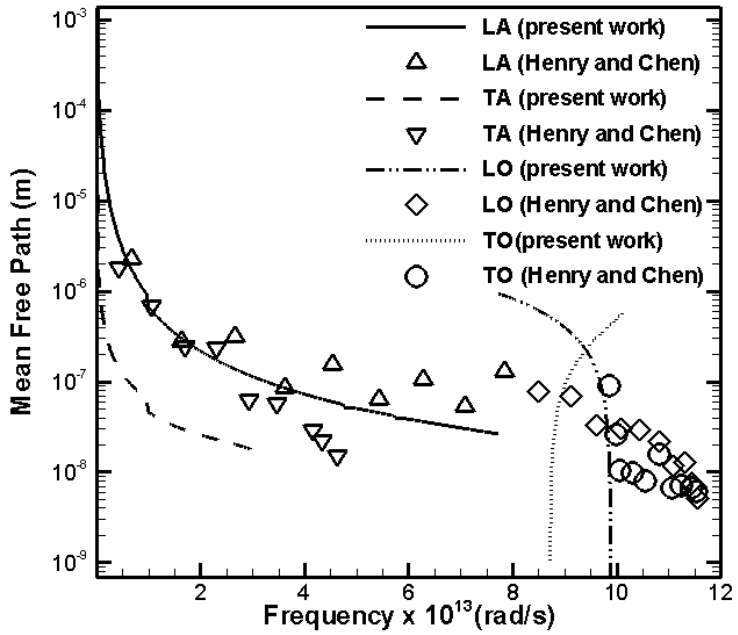


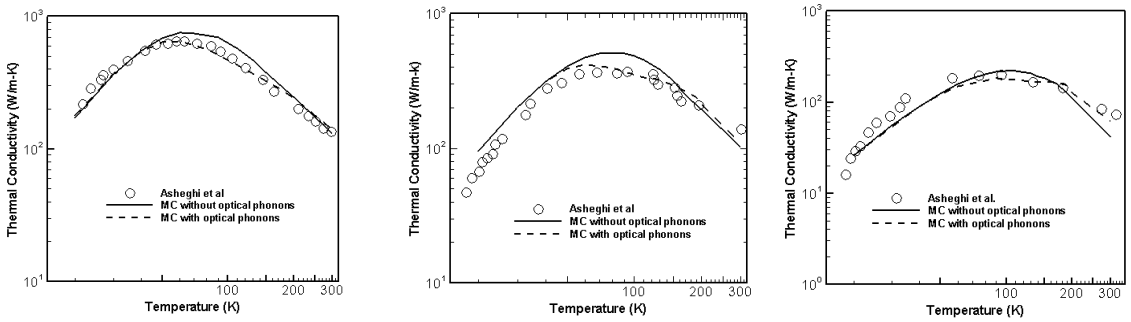
Figure 1: Comparison of mean free paths of all four phonon modes at 300 K computed using the present approach, and data obtained using molecular dynamics by Henry and Chen [3].

Monte Carlo Simulations

A three-dimensional Monte Carlo based solver for the BTE for phonons was developed. The starting point for development of this Monte Carlo code was an existing code developed by Mazumder and Majumdar [4]. This code was modified to include three-dimensional transport. It was also modified to include the optical phonon modes. Finally, the scattering algorithm was modified to ensure that Kirchoff's law is obeyed, following the algorithm proposed by Lacroix *et al.* [5].

The results of the Monte Carlo simulations were compared against measured data for thermal conductivity of silicon thin films, and selected results are shown in Fig. 2. It is clear that the inclusion of optical phonons does have an effect on the predicted thermal conductivity of silicon thin films. At low temperature (< 50K), thermal conductivity predictions are dominated by boundary scattering. Thus, inclusion of optical phonons has no impact on the predicted thermal conductivity. At intermediate temperatures (50-200K), the occupation number of optical phonons is quite low. Few optical phonons are present, and they carry little energy themselves. However, they decrease the scattering time-scales of the acoustic phonons *via* collisions, thereby resulting in a decrease in the value of thermal conductivity. At high temperature (> 200K), optical phonons are excited, and a significant

fraction of the energy is carried by optical phonons themselves. Thus, their inclusion enhances the thermal conductivity, and is evident from the 0.42 μm data for 300K. It is also noteworthy that the high-temperature effect is more pronounced in thin films (0.42 μm) than in thick films (3 μm). For example, for a 3 μm film at 300K, collisions between phonons is so abundant that it does not matter what phonons are considered in the simulation because transport is almost in the diffusion regime. The alteration of thermal conductivity shown by these results discounts earlier assumptions [4] that optical phonons can be neglected for silicon thin film thermal conductivity prediction.



3 μm film 1.6 μm film 0.42 μm film

Figure 2: Predicted and measured [6] through-plane thermal conductivity for silicon films of various thicknesses

Development of Deterministic Methods for Solving the BTE for Phonons

On account of the six-dimensional nature of the BTE, it is computationally very expensive to solve. The Monte-Carlo method is often used, but is prohibitive for simulation of heat transport in practical engineering devices, and deterministic methods for solving the BTE are desirable. One popular deterministic approach to solve the BTE is the discrete ordinates method. However, the discrete ordinates method exhibits inaccuracy in the form of so-called "ray effects" [7], as clearly seen in Fig. 4. To alleviate this effect, in this project, we developed a new hybrid formulation for solving the BTE based upon the ballistic-diffusive idea originally proposed by Chen [8], which in turn, is based upon its counterpart in photon (radiation) transport. The approach involves splitting the total phonon flux into two components: a ballistic wall-emitted component and a diffusive media component. Traditionally, the ballistic component is solved using a viewfactor approach, which is tedious and expensive. In this work, the solution to the ballistic component is obtained using the Discrete Ordinates Method (S_N approximation), while the diffusive component is obtained by applying the first order spherical harmonics method (or P_1 approximation). Both equations were solved using the finite-volume procedure on an unstructured mesh, making the method amenable to use in complex three-dimensional geometries. The new method was tested for solution of the gray phonon BTE in two-dimensional geometries over a large range of acoustic thicknesses (Knudsen numbers). The results are compared against both standalone DOM-BTE and benchmark Monte Carlo results. Fig. 3 shows a test problem that was simulated.

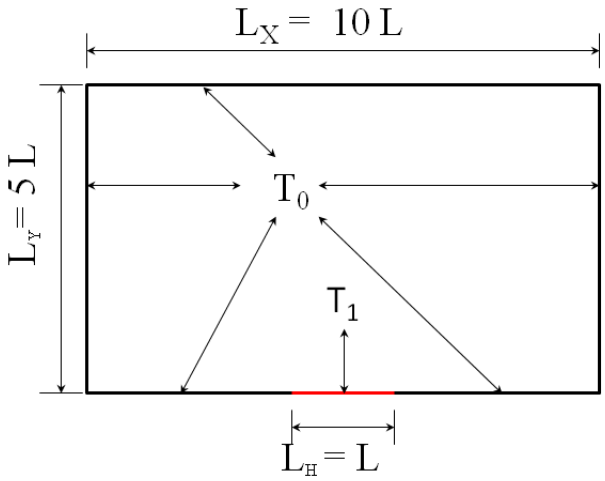


Figure 3: Geometry and boundary conditions for test problem: T_1 represents are heater, while the other walls are colder.

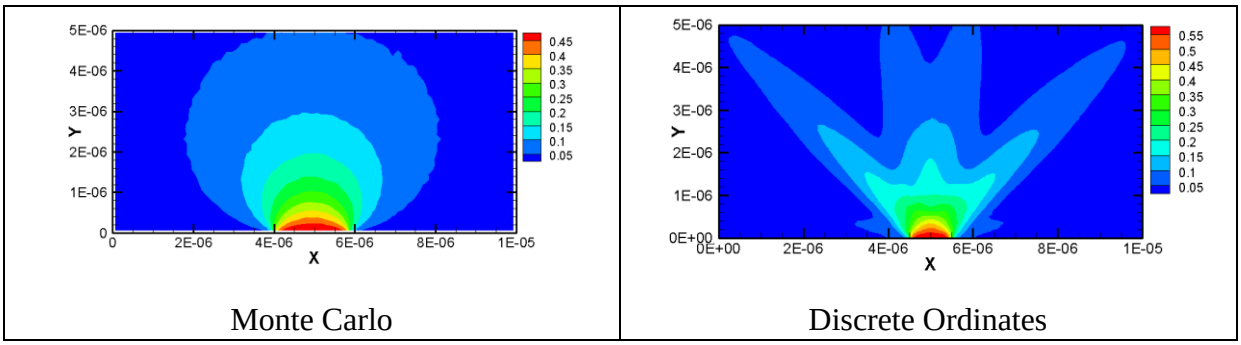


Figure 4: Non-dimensional temperature distributions computed using the Monte Carlo method and the discrete ordinates method at non-dimensional time of 100 and Knudsen number of 10. The discrete ordinates method clearly shows so-called "ray effects" [7].

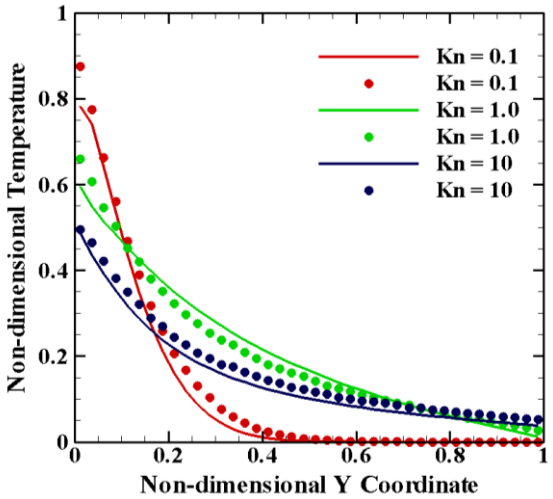


Figure 5: Centerline non-dimensional temperature distribution computed using the new hybrid S_N-P_N method at non-dimensional time of 100 and various Knudsen numbers. The dots represent benchmark Monte Carlo results, while the solid lines represent hybrid S_N-P_N method results.

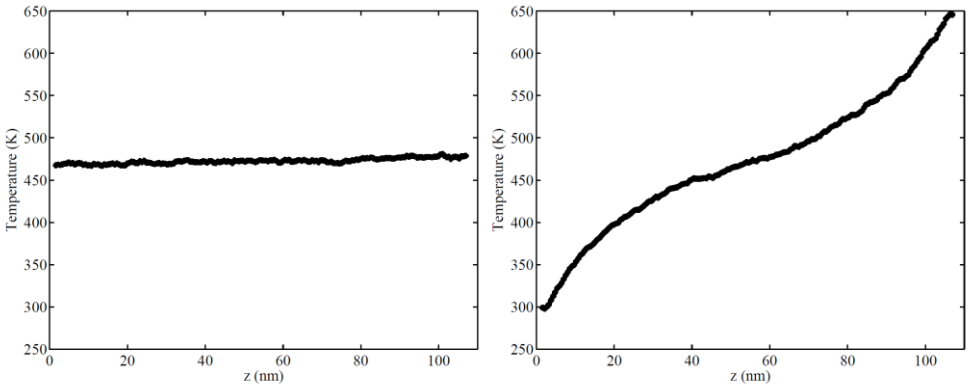
Molecular Dynamics Simulations

Two methods were applied to calculate the thermal conductivity of silicon nanowires. One was to apply the Green-Kubo formula to an equilibrium system. The other was to use Non-Equilibrium Molecular Dynamics (NEMD). In NEMD method, heat current is introduced by heating one end of the nanowire while cooling the other. A steady heat flow would be reached, causing a temperature gradient along the axis. The nanowire is divided into many slices along the axial direction, in each of which a local temperature is defined by average of kinetic energies (although it is a non-equilibrium simulation, each slice can be in local equilibrium and instantaneous local temperature can be defined as long as each slice has more than 30 atoms). We used the Stillinger-Weber (SW) potential in predicting thermal conductivity of silicon. Two-body and three-body interaction terms are included in the SW potential. The potential parameters were fitted so that the diamond structure is the most stable structure at low pressure compared to simple alternatives such as simple cubic, fcc and bcc. Melting point and liquid structure were also taken into account in the fitting process. SW potential has been tested for predicting lattice vibrational properties in the literature where elastic constants, dispersion relations, thermal expansion coefficients and thermal conductivities of bulk silicon are calculated. Both Kluge et al. [9] and Cowley [10] reported that C_{12} of bulk silicon given by SW potential were overestimated by around 20% while C_{44} underestimated by about 30%. Cowley [10] also showed that SW potential is better than the Tersoff potential in predicting elastic constants and dispersion curves. Broughton et al. [11] compared phonon dispersion curves of bulk silicon given by SW potential model to those by experiments. They found that dispersion relations of high frequency modes of transverse acoustic branches were overestimated, i.e., they had higher group velocities (steeper slopes) and higher cut-off frequencies than experimental curves. Chantrenne et al. [12] showed a similar result except that in their case [100] longitudinal acoustic curve was also overestimated. Thermal expansion is a result of anharmonic parts of interaction among particles. Thus by evaluating thermal expansion coefficients some authors tried to test how well SW potential can describe the anharmonic interaction. Chantrenne et al. [12] plotted atomic volume with respect to temperature curves given by SW potential and by experiments, and found that the two curves were very close. Therefore the authors concluded that SW potential could give good prediction for thermal expansion coefficients. Porter et al. [13] also showed that SW potential gave better description of thermal expansion coefficients versus temperature relation than Tersoff potential and a hybrid potential. But they proposed that it was not because SW potential better took account of anharmonic properties but due to a cancellation of errors in predicting Grüneisen parameter for the acoustic and optic modes. They concluded that all the three potentials gave poor predictions of Grüneisen parameters, which they thought were more fundamental parameters than thermal expansion coefficients in examining anharmonic properties of an empirical potential.

Several authors reported their results on thermal conductivities of bulk silicon based on SW potential model. Volz et al. [14] employed equilibrium MD simulation to calculate thermal conductivity of bulk silicon crystal. Their results have good match with experiments on isotopically enriched silicon. Schelling et al. [15] described their non-equilibrium and equilibrium MD simulations in predicting thermal conductivity of bulk silicon based on SW potential. Their results of 65 ± 16 W/mK from NEMD and 62 ± 16 W/mK from EMD at 1000

K can be compared to extrapolated experimental value of about 50 W/mK. The result of 119 ± 40 W/mK at 500 K from NEMD matches well with the extrapolated experimental value of about 120 W/mK. To sum up, although SW potential may not give accurate description of anharmonic parts of interaction, it is certainly the most widely used empirical potential in predicting thermal conductivity of silicon and the results on bulk silicon have turned out to be in good match with experimental data.

In our NEMD simulation, the time step is chosen to be 0.383 fs. Free boundary conditions in three directions are applied. Before introducing heat current, 3000000 steps (1.15 ns) take place to relax the structure. Figure 6 shows the temperature distribution with and without heat current. The non-linear dependence of temperature on the position at the two ends of the nanowire is due to the scattering of phonons at the heat source and sink. Therefore, to calculate the thermal conductivity by Fourier's Law, a segment in the middle of the nanowire is extracted. A temperature profile of such a segment is shown in Fig. 7. The thermal conductivity of the nanowire is then obtained by inverting Fourier's law.



(a) No heat current is introduced (b) Heat current is introduced

Figure 6: Temperature gradient along [100] direction of the nanowire (3 × 3 × 200). Temperature fields in both plots are averaged over 3000000 time steps (1.15 ns). The mean temperature of (a) is 472.6 K, while (b) is 471.8 K.

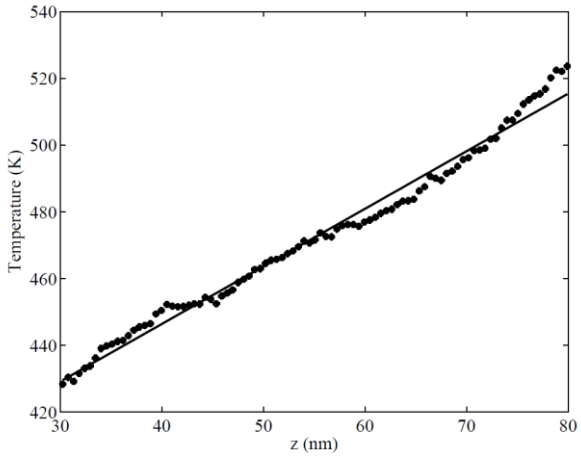


Figure 7: Temperature profile of 3×3×200 silicon nanowire between z = 30 nm and z = 80 nm. The total length of the nanowire is 108 nm. $\Delta\varepsilon = 1 \times 10^{-4}$ eV.

Several kinds of nanowire geometries were simulated. These include nanowires with circular

and square cross-sections, and with and without tapering (change in cross-sectional area).
For the square cross-section nanowires, it was found that:
1) Given that the cross-sectional area is fixed, the length of the nanowire does not significantly affect the thermal conductivity.
2) Given that the length of the nanowire is fixed, thermal conductivity increases with larger cross-sectional area of Si nanowire.
3) Given the exact same size of the nanowire, if we change the heating rate, that is the amount of the energy added and extracted from either end of the nanowire is changed, no significant change in the thermal conductivity is found.
The results are summarized below in Table 1.

Table 1: Thermal conductivity of Si nanowires with square cross-section and with different parameters

Length (nm)	100	200	100	100
Cross-section (nm^2)	5.43 x 5.43	5.43 x 5.43	10.86 x 10.86	5.43 x 5.43
Heating rate (J/s)	1.6e-7	1.6e-7	1.6e-7	1.6e-6
Thermal-conductivity (W/m/K)	14.49	12.66	27.52	12.77

For nanowires with a circular cross-section, the following results were found:
1) Given that the length of the nanowire is fixed, thermal conductivity significantly reduces with smaller diameter of Si nanowire.
2) Given the exact same size of the nanowire, if we change the heating rate, i.e., the amount of the energy added and extracted from either end of the nanowire is changed, no significant change occurs.
The results are summarized below in Table 2.

Table 2: Thermal conductivity of Si nanowires of circular cross-section with different parameters

Length (nm)	100	100	100
Diameter (nm)	5	10	5
Heating rate (J/s)	1.6e-7	1.6e-7	1.6e-8
Thermal-conductivity (W/m/K)	1.91	16.61	1.99

From comparison between the two nanowire geometries, it is found that for the two different model, even if we have the same length (100 nm) and approximately same cross section (size = 5.4 nm and diameter = 5 nm), the calculated thermal conductivity are significantly different, as summarized in Table 3. It is seen from Table 3 that for the approximately same diameters, cubic nanowire gives a result which is much larger than that of cylindrical nanowire. This suggests that in addition to the raw size scale, detailed cross-sectional shape and surface conditions can significantly affect the thermal conductivity of nanowires, which supports the experimental findings of Boukai et al. [16] and Hochbaum et al. [17]. Similar conclusion was also drawn by Donadio and Galli [18], where an atomically thin layer of surface

amorphous material was found to influence thermal conductivity of Si nanowires greatly. Therefore, nano-structuring and surface treatments offer real possibilities in controlling the thermal conductivities of low-dimensional semiconductor nanostructures.

Table 3: Comparison between the cubic and cylindrical model

Model	Square	Circular	Square	Circular
Length (nm)	100	100	100	100
Size / Diameter (nm)	5.4	5	10.9	10
Heating rate (J/s)	1.6e-7	1.6e-7	1.6e-7	1.6e-7
Thermal-conductivity (W/m/K)	14.49	1.91	27.52	16.61

In addition to silicon nanowires, we have also investigated the lattice vibrational and thermal conduction properties of carbon-based nanostructures such as grapheme [19]. It was found that elastic strain can have a large effect on the vibrational properties of these materials. Since nanostructures can sustain a much larger dynamical range of elastic stress and strain without relaxation (so-called "ultra-strength" [20] property) than coarse-grained materials, our work suggests one can develop elastic-strain-engineering [20] approaches to tune the thermal conduction and thermoelectric properties of semiconductor nanostructures.

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List of papers (already published, in press, submitted, in preparation) as a direct result of this project

- "Monte Carlo Study of Phonon Heat Conduction in Silicon Thin Films Including Contributions of Optical Phonons," (2010), A. Mittal, and S. Mazumder, *Journal of Heat Transfer*, Vol. 132(5), Article number 052402
- "Monte Carlo Study of Phonon Heat Conduction in Silicon Thin Films: Role of Optical Phonons," A. Mittal and S. Mazumder, *Proceedings of the ASME Summer Heat Transfer Conference*, July 19-23, 2009, San Francisco, CA, Paper Number HT2009-88008
- "A Hybrid S_N-P_N Formulation for Solution of the Boltzmann Transport Equation for Phonons," A. Mittal and S. Mazumder, *Proceedings of the Joint ASME/JSME Thermal Engineering Joint Conference*, Honolulu, HI, March 2011, Paper number AJTEC2011-44129
- "General Ballistic-Diffusive Formulation and Hybrid S_N-P_N Solution of the Boltzmann Transport Equation for Phonons," A. Mittal and S. Mazumder, *Journal of Heat Transfer*, in preparation
- "Sensitivity of Silicon Nanowire Thermal Conductivity to Surface Conditions," Wei Liu, Zheng Li and Ju Li, in preparation

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- "Monte Carlo Study of Phonon Heat Conduction in Silicon Thin Films Including Contributions of Optical Phonons," (2010), A. Mittal, and S. Mazumder, *Journal of Heat Transfer*, Vol. 132(5), Article number 052402

- "Monte Carlo Study of Phonon Heat Conduction in Silicon Thin Films: Role of Optical Phonons," A. Mittal and S. Mazumder, *Proceedings of the ASME Summer Heat Transfer Conference*, July 19-23, 2009, San Francisco, CA, Paper Number HT2009-88008
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