Multiscale phonon blocking in Si phononic crystal nanostructures

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In-plane thermal conduction and phonon transport in both single-crystalline and polycrystalline Si two-dimensional phononic crystal (PnC) nanostructures were investigated at room temperature. The impact of phononic patterning on thermal conductivity was larger in polycrystalline Si PnCs than in single-crystalline Si PnCs. The difference in the impact is attributed to the difference in the thermal phonon mean free path (MFP) distribution induced by grain boundary scattering in the two materials. Grain size analysis and numerical simulation using the Monte Carlo technique indicate that grain boundaries and phononic patterning are efficient phonon scattering mechanisms for different MFP length scales. This multiscale phonon blocking structure covers a large part of the broad distribution of thermal phonon MFPs and thus efficiently reduces thermal conduction.

I. INTRODUCTION

Nanoscale heat transport has recently been investigated because of its importance both in fundamental physics and practical applications1,2. Characteristic phonon transport phenomena have been reported in a variety of systems such as semiconductor super lattices3,4, membranes containing nanoparticles5, porous nanostructures6-8, nanowires9, and phononic crystal (PnC) structures10-13. The phonon mean free path (MFP) is the most important physical parameter for determining the thermophysical property of a system. The thermal conductivity of a crystal in a bulk material is reduced when the characteristic length of the system becomes comparable to or shorter than the phonon MFP in the bulk material. In such a system, the thermal property no longer follows the Fourier law but instead is described by semiballistic phonon transport. Phonon transport physics is especially interesting in PnC nanostructures because the wave nature of phonons appears14 where coherence is preserved, and together with the incoherent phonon scattering process15, determines phonon transport.

Thermoelectrics is an important application, in which phonon transport nanoengineering plays an active role. The figure of merit $ZT$ is given by $S^2\sigma T/\kappa$; where $T$ is temperature, $S$ is the Seebeck coefficient, $\sigma$ is electrical conductivity, and $\kappa$ is thermal conductivity. The concept of “phonon-glass and electron-crystal” proposed by Slack yields the following strategy for increasing $ZT$: reduce thermal conduction while maintaining electrical conduction by taking advantage of different phonon and electron MFPs16. Many groups have demonstrated very low values of thermal conductivity by increasing phonon scattering in a variety of nanostructures17. However, for this purpose, it is important to be aware that thermal phonons are distributed over a broad range of frequencies17,18, and thus there is a multiscale distribution of thermal phonon MFPs. Therefore, a phonon blocking mechanism that covers the whole MFP range is required in order to reduce thermal conductivity efficiently. Biswas et al. demonstrated the validity of this idea using an all-scale hierarchical architecture in which three different scattering mechanisms blocked phonon transport and covered different thermal phonon MFP ranges from the atomic scale to the mesoscale by using PbTe (Ref. 19).

Si is considered one of the most promising candidates of a high performance thermoelectric material with a low environmental load. Therefore, it is important to investigate the validity of the strategy for Si and to obtain quantitative information for structural design.

In this study, we investigated the use of all-scale hierarchical architecture in Si for efficient reduction of thermal conduction. We fabricated two-dimensional (2D) PnC nanostructures using both single-crystalline and polycrystalline Si membranes and measured thermal conductivity at room temperature. In the polycrystalline Si PnC nanostructures, grain boundary scattering blocked thermal phonons with relatively short MFPs, and phononic patterning blocked phonons with longer MFPs. We discuss the validity of multiscale phonon blocking in Si, using grain size analysis data and numerical simulation results generated via a Monte Carlo technique.

II. EXPERIMENTAL DETAILS

The PnC nanostructures were fabricated with either single-crystalline or polycrystalline Si membranes. For single-crystalline Si samples, we used a commercially available (100) nominally boron-doped silicon-on-insulator wafer with a 145 nm-thick upper Si layer and a 1 μm-thick SiO2 buried oxide layer. For polycrystalline Si samples, the top polycrystalline Si layer was grown on a 1.5 μm-thick SiO2 layer on a (100) Si wafer by low-pressure chemical vapor deposition at 625 °C. The layer was undoped and was 143 nm thick, as measured by ellipsometry. The PnC nanostructures were formed via electron beam (EB) lithography using a reactive ion etching/inductively coupled plasma system, with SF6/O2 gas as the etchant. The oxide layer under the Si layer was removed with hydrofluoric acid in order to form the air-bridge structures. The dimensions of the PnC nanostructures were measured by scanning electron microscopy (SEM).

Figure 1(a) shows an SEM image of the whole air-bridge structure with the 2D PnC structures. In the center of the air-bridge structure, a 125 nm-thick Al layer was deposited to form a $4 \times 4 \mu m^2$ pad on the Si layer to enable thermoreflectance
measurements. The central Si island with the Al pad atop was then supported by two PnC structures. The width and the length of the structure were 5 \( \mu \)m and 25 \( \mu \)m, respectively. The 2D PnC structures were formed using circular air holes periodically aligned as a square lattice, as shown in Fig. 1(b). PnC structures with a variety of radii were fabricated with a fixed period \( a = 300 \) nm.

To measure in-plane thermal conductivities of the PnC nanostructures, a method using micro time-domain thermoreflectance (\( \mu \)-TDTR) was developed, which has very high throughput as compared to electrical methods. The principle of this technique is the same as that for TDTR\(^{20}\); however, it can be applied to micrometer-sized systems. The Al pad was heated by a quasicontinuous laser beam (wavelength \( \lambda = 642 \) nm) for 500 ns, and the temporal evolution of the temperature of the Al pad (the TDTR signal) was monitored by a continuous-wave laser beam (\( \lambda = 785 \) nm). Both beams were collinearly focused on the Al pad, as shown in Fig. 2(a), by using a microscope objective lens with a numerical aperture of 0.65. The beam spot on the pad was approximately 700 nm in diameter. The power of the pump pulse was set so the temperature increase was less than 5 K in the Al pad, and it was verified that the pump power did not change the thermal conductivity in the range of temperature increase. We calculated the radiation loss by Stefan-Boltzmann law and verified that the radiation loss is negligible under this experimental condition. All the measurements were performed at room temperature and in a vacuum chamber to eliminate heat-convection loss. The PnC nanostructures that supported the central Si island were the only heat dissipation channels. This well-defined system made it possible to obtain a highly reliable value of the thermal conductivity by analyzing the temporal evolution of the TDTR signal. The temperature evolution in whole structure was simulated via the finite element method (FEM) by using COMSOL Multiphysics\(^{5}\). Figure 2(b) shows the simulated temperature distribution, 15 \( \mu \)s after pulse heating, for a PnC structure with \( a = 300 \) nm and \( r = 115 \) nm.

### III. EXPERIMENTAL RESULTS

For both single-crystalline and polycrystalline samples, the thermal conductivity of the PnC nanostructure was measured by \( \mu \)-TDTR at room temperature. Figure 3 shows TDTR signals for single-crystalline PnCs with \( r = 73 \) nm, 115 nm, and 126 nm, as well as for an unpatterned membrane. The dots and the solid lines represent experimental and simulated TDTR traces, respectively. The increase in the TDTR signal was caused by the temperature increase in the Al pad from the heating pulse, which was applied from time \( t = 0 \) to \( t = 500 \) ns. The heat was only dissipated through the PnC nanostructures, and the temperature of the Al gradually decreased on a timescale on the order of tens of microseconds. The best fitting curve for each PnC with \( r = 73, 115, \) and 126 nm, as well as for the unpatterned membrane, is given by thermal conductivities of 41 Wm\(^{-1} \)K\(^{-1} \), 35 Wm\(^{-1} \)K\(^{-1} \), 29 Wm\(^{-1} \)K\(^{-1} \), and 75 Wm\(^{-1} \)K\(^{-1} \), respectively.

The thermal conductivity of the unpatterned membrane is similar to the reported value for a single-crystalline Si membrane of the same thickness\(^{22} \), thus confirming the reliability of the measurement and analysis.
phonons and that the system was in the semiballistic phonon transport regime. We found that forming air holes, even when the value of $r/a$ was small, dramatically reduced thermal conductivity. This result indicates that the side walls of the air holes, which are perpendicular to the direction of in-plane phonon transport, backscatter phonons and largely reduce thermal conductivity\textsuperscript{7}. For single-crystalline Si, the thermal conductivity showed a steep reduction above the value of $a = 2r$, the necking effect\textsuperscript{7} became more effective and dramatically reduced thermal conductivity. This tendency had also been observed in our previous measurements for Si nanowires\textsuperscript{8,9}.

For polycrystalline PnC structures, the measured thermal conductivity for the membrane was 11 Wm\textsuperscript{-1}K\textsuperscript{-1}, and for PnCs with $r = 82$ nm, $98$ nm, and $123$ nm, the thermal conductivity was $5.0$ Wm\textsuperscript{-1}K\textsuperscript{-1}, $4.7$ Wm\textsuperscript{-1}K\textsuperscript{-1}, and $4.3$ Wm\textsuperscript{-1}K\textsuperscript{-1}, respectively. The radius dependence was similar to that of the single-crystalline samples, but the impact of the phononic patterning was different because of the different thermal phonon MFP distributions. The magnitudes of the reduction in thermal conductivity for single-crystalline and polycrystalline Si PnCs can be compared by considering the data around $r = 100$ nm, where the necking effect is moderate. By interpolating the experimental plots, the thermal conductivities at $r = 100$ nm plots were estimated as $38$ Wm\textsuperscript{-1}K\textsuperscript{-1} and $4.66$ Wm\textsuperscript{-1}K\textsuperscript{-1} for the single-crystalline and the polycrystalline samples, respectively. The magnitudes of the reductions in membrane thermal conductivity were $49\%$ and $58\%$, respectively. This indicates that the impact of the phononic patterning is larger for polycrystalline Si PnC nanostructures than for single-crystalline nanostructures.

To quantify the multiscale phonon blocking, thermal conductivity accumulation functions for bulk Si and for single-crystalline Si PnC nanostructures were calculated. In nanostructures, MFPs of phonons are shortened due to phonon boundary scattering. By defining the effective MFP as $\Lambda_{\text{eff}}$, thermal conductivity in terms of Boltzmann transport can be written as

$$\kappa = \frac{1}{3} \sum_{q, s} c_{q, s} v_{q, s} \Lambda_{\text{eff}, q, s},$$

where $c$ and $v$ are the specific heat and group velocity, which depend on phonon wave vector $q$ and branch $s$.

The calculation of $\Lambda_{\text{eff}}$ was realized using a Monte Carlo ray tracing simulation. The simulation reproduces the single-crystalline Si PnC nanostructures in the experiment [Fig. 1(b)] by taking a square unit cell (side $a = 300$ nm) with an air hole in the center. The thickness of the unit cell was $150$ nm. $N$ unit cells were arranged in a row in the direction parallel to heat flux ($x$ direction), and periodic boundary condition was imposed in the other in-plane direction ($y$ direction).

The method calculates the phonon transmission probability ($r$) by emitting a phonon from one side of the nanostructure ($x = 0$) with an incident polar ($\theta$) and azimuthal ($\phi$) angles, and statistically evaluating the probability of phonons to reach the

![FIG. 4. (Color online) Measured thermal conductivities for a variety of radii in single- (red circles) and polycrystalline (blue circles) Si PnC nanostructures.](image)

![FIG. 5. TEM images of (a) top and (b) cross-sectional views for the poly-Si wafer. (c) Histogram of the grain size measured on the surface. The grain size at the bottom part is much smaller due to the conical shape of the grains.](image)
other side ($x = N_a$). When the phonon arrives at the out-of-plane boundaries or the surface of the air holes, it is scattered (reflected) fully diffusely. In addition, the phonon is scattered by phonon-phonon scattering i.e. it changes the direction randomly after traveling a distance $\Delta h = R$ from the location of the previous scattering. Here, $\Lambda$ is the MFP of the phonon in bulk single crystal and $R$ is a random number between 0 and 1. As the value of $r$ exhibits the size effect when the phonon MFP is longer than the length of the simulated system $L = N_a$, $L$ was chosen to be sufficiently large to obtain a converged value.

The transmission probability $r$ was calculated for a range of $\Lambda$. For each value of $\Lambda$, simulations scan over the polar angles $\theta$ [0, $\pi/2$] discretized into regular intervals ($\pi/180$), while the azimuthal angle $\phi$ and the $y$-z coordinates of emission are randomly chosen with uniform distributions. The simulations were performed 96,040 times for each value of $\theta$, and the values of $r$ were averaged. $\Lambda_{\text{eff}}$ can then be obtained based on kinetic theory and Landauer's formula as,

$$\Lambda_{\text{eff}} = \frac{3L}{2M} \int_0^{\pi/2} r(\theta, \Lambda) \cos \theta \sin \phi d\phi d\theta,$$

where $M$ is a modification factor of the structure accounting for the porosity of PnC structures calculated by COMSOL Multiphysics®.

Equation (2) shows that the dependence of $\Lambda_{\text{eff}}$ on $q$ and $s$ ($\Lambda_{\text{eff},q,s}$) can be obtained by the dependence of $\Lambda$ on $q$ and $s$ ($\Lambda_{q,s}$). $\Lambda_{q,s}$ here was obtained by lattice dynamics calculation of bulk Si at room temperature using the interatomic force constants from first principles. Finally thermal conductivity of the single-crystalline Si PnC nanostructures was calculated by substituting $\Lambda_{\text{eff},q,s}$ into Eq. (1). We also calculated thermal conductivity of the Si membrane without the holes (i.e. $r = 0$) and confirmed agreement with the analytical solution of Boltzmann transport equation.

Figure 6(a) shows the thermal conductivities (squares) calculated using the data for single-crystalline Si structures. The radius dependence of the calculated thermal conductivities reproduces the same tendency and nearly the same values. Figure 6(b) shows the calculated thermal conductivity accumulation functions for bulk Si and for single-crystalline Si PnC nanostructures with $r = 30$ nm, 90 nm, and 135 nm. The vertical coordinate of any point on the function represents the thermal conductivity of a phonon whose MFP is less than the horizontal coordinate of that point. The surface scattering by the PnCs shortens the $\Lambda_{\text{eff}}$ of phonons which have MFPs that are longer than the neck size in the unpatterned membrane and shifts the distribution functions to the shorter side. Note that the thermal conductivity accumulation is almost saturated around sizes that are similar or a few times longer than the neck size.

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