Control of Phonon Transport by Phononic Crystals and Application to Thermoelectric Materials

Masahiro Nomura1,2,3

1 Institute of Industrial Science, The University of Tokyo, Tokyo 153–8505, Japan
2 Institute for Nano Quantum Information Electronics, The University of Tokyo, Tokyo 153–8505, Japan
3 JST, PRESTO, Kawaguchi 332–0012, Japan

Phonon transport and thermodynamic properties of nanostructured materials have been investigated and utilized to improve thermoelectric performance for various materials. In nanostructures, phonon transport is completely different from that in bulk materials and results in dramatic enhancement in the thermoelectric performance. This article reviews the impact of nanostructuring on the phonon transport and mainly focuses on phononic crystal nanostructures, in which the wave nature of phonons also plays an important role. We demonstrate that it is important to efficiently scatter thermal phonons, which distribute to wide range of frequencies, with different phonon scattering mechanisms in the spatial domain. We also demonstrate an enhancement of thermoelectric property of polysilicon thin films by phononic crystal patterning.

Keywords: phonon transport, phononics, phononic crystal, thermoelectrics

1. Introduction

Generally, in the case of solids the material is assumed large and homogenous enough that the thermal conductivity can be treated as simple heat diffusion. These heat carriers are either electrons or quantized lattice vibrations called phonons. In the case of metals, the majority carrier is the electron while, for semiconductors, the majority carrier is the phonon. In nanostructures, since the size of the system is equivalent to the mean free path (MFP) of the carrier, in order to more clearly understand the phenomenon of thermal conductivity we must consider the ballistic transport of phonons without describing their behavior as a diffusion process. Ballistic phonon transport, as well as characteristic phonon transport due to scattering caused by the structure, has been reported in various structures including atomic scale carbon nanotubes1), graphene2), semiconductor super lattices3,4), structures containing nano particles5,6), porous structures7,8), nanowires9) and phononic crystal (PnC) structures10–16). Since the thermal conductivity in nanostructures is system-dependent, using certain materials it is possible to fabricate monolithic devices with various thermal conductivities. Also, since it is now possible to remarkably decrease the characteristic thermal conductivity of the materials by nanofabrication, new choices are available for developing thermoelectric conversion materials17,18). Using the difference in length of the MFP of electrons and phonons, it is possible to dramatically decrease the thermal conductivity of a material without negligibly affecting the electrical conductivity. This approach was meant to emphasize the difference between electric charge and heat carriers, which means that the system is no longer restricted by the Wiedmann-Franz Law, which governs the temperature dependent ratio of thermal conductivity to electrical conductivity in metals19). Until now, many have reported on a variety of materials with a high figure of merit for thermoelectric conversion by implementing nanostructuring in harmless and inexpensive materials with extremely low ZT values and in bulk materials that already possessed a high ZT value. Figure 1 shows scanning electron microscope (SEM) and tunneling electron microscope (TEM) images of various systems reporting such findings. Components that change the lattice thermal conductivity can be, as shown in Fig. 2, either classified as incoherent scattering processes such as impurity, surface, interface and phonon-phonon scattering under the particle description, or as coherent scattering processes based on the wave description resulting from periodic PnC for acoustic waves. In order to analyze these phenomena, the former uses the relaxation time τ which becomes necessary when approximating scattering processes and is taken from the Boltzmann transport equation which serves as the foundation for classical transport theory (Fig. 2). In this equation, f0 and f are the phonon distribution functions in equilibrium and non-equilibrium states, and v is the velocity vector. The latter analyzes

phonon transport and calculates the phononic band diagram using finite element method under Floquet conditions for the shape, density and young modulus of the periodic structure. The governing equation in the coherent scattering regime is given by the elastodynamic wave equation in Fig. 2:

\[ u = \text{displacement vector}, \quad \rho = 2329 \text{ kg m}^{-3} \text{ as the mass density,} \]
\[ \lambda = 84.5 \text{ and } \mu = 66.4 \text{ GPa as the Lame parameters for the case of silicon. Much like with the Knudsen number used in fluid dynamics, we must keep in mind the characteristic length of the system as well as the MFP when discussing heat transport. Thermal conduction in the incoherent and coherent regimes is based on different concepts: reduction of phonon relaxation time and reduction of the group velocity are the key factors in respective regime.}

In this paper, we provide a great example of thermal conductivity in silicon PnC nanostructures exhibiting both semi-ballistic transport and wave nature of photons and which are described by both the particle and wave descriptions. In addition, we will discuss our current progress in thermoelectric conversion and the control of heat conductivity in multiscale polysilicon designed while considering the multiscale nature of phonons.

2. Experimental Method

2.1 Micro-thermoreflectance method

Typically, the thermal conductivity of mesoscale materials is taken using electrical methods. With our measurement technique, we are able to detect small changes in temperature and measure thermal conductivity more precisely; however, it takes a long time to fabricate the samples, the environmental footprint is high and the throughput is quite low. Since we will need to conduct measurements on various PnC structures, we have developed an optical measurement technique called micro-thermoreflectance which has much higher throughput than the existing electrical methods. Time domain thermoreflectance (TDTR) is a method for measuring the thermal conductivity of thin film materials on which metal has been deposited by observing the change in temperature over time after using a pulsed laser to heat the film. Then, the experimental temporal evolution can be compared with simulation results. Our custom-made micro-TDTR setup can measure in-plane thermal conductivity in micro/nano structures using focused pump and probe laser beams. The metal layer converts the light to thermal energy, effectively acting as a transducer to detect temperature change by observing changes in reflectance.

In our experiment, as shown schematically in Fig. 3(a), we have devised a sample structure and focused light that we can apply to a micro-scale system. By making a suspended structure from the active silicon layer of an SOI wafer, we form a central island which holds the aluminum pad and supports our structure on all sides. With such an arrangement, we can ensure that heat dissipation will occur through only the structure to be measured, thus allowing us to compare with simulation data and obtain thermal conductivity values at high precision. The wavelength of the excitation source and probe laser source were 642 nm and 785 nm respectively, and the dot of focused light had a diameter of approximately 0.7 μm. We chose the wavelength of the probe laser so that the thermal reflectance coefficient, measured in percent change in reflectance per unit change in temperature of the aluminum pad, would be large enough. The coefficient value in our experiment was 0.015% K. Since thermal conductivity is temperature dependent, it is desirable to heat the PnC structures as little as possible. In our experiment, we adjusted the pump laser power so that the increase in temperature remained below 2 K and confirmed that the thermal conductivity was consistent within that range of temperature increase. In addition, the measurement took place in a vacuum so that air would not affect the heat dissipation in the channel which we are trying to measure.

The dimensions of the nanostructure were precisely verified using SEM and the simulation using finite element method was designed based on these dimensions. Using the thermal conductivity \( \kappa \) as the only variable, we compared with the values obtained from the TDTR signals using the technique.
described above, and derived the most appropriate thermal conductivity coefficient for our simulation. The physical model, as also seen in eq. 1, expresses an effective thermal conductivity for the entire device which only considers the decrease in thermal conductivity by surface scattering as a result of heat transfer.

\[
\rho C_p \frac{\partial T}{\partial t} - \kappa \Delta T = Q(t)
\]

The material used was single crystal Silicon with a density \( \rho \) of 2329 kg/m\(^3\), a specific heat at constant pressure \( C_p \) of 700 J/kg·K and a time dependent heat quantity per unit volume given by the heating pulsed laser source \( Q(t) \) measured in W/m\(^3\). Consistent with the experiment, energy was supplied to the aluminum pad in a Gaussian distribution from time \( t = 0 \) to 500 ns. We can determine the thermal conductivity via the least squares method by comparing the aluminum pad surface temperature simulation curve with our experimental results using thermal conductivity as the parameter. The TDTR signals (dots) from the 2D PnC nanostructure, which we will introduce in the next section, and the simulation curve (solid line) are shown in Fig. 3(b) and have produced extremely reproducible results.

### 2.2 Sample fabrication

Beginning with either an SOI wafer on the market or a wafer fabricated using low pressure chemical vapor deposition system, we fabricated the suspended structure necessary to measure the thermal conductivity by micro-thermoreflectance technique in PnC nanodevices like in Fig. 4(a). Then, using electron beam lithography and dry etching, the single crystal silicon nanostructures contained a 145 nm active layer above a 1 \( \mu \)m buried oxide layer, while the polysilicon nanostructures were fabricated on a silicon board with a 143 nm polysilicon crystal thin film grown by low pressure chemical vapor deposition system on top, and a 1.5 \( \mu \)m SiO\(_2\) layer above that. A 125 nm thick, \( 4 \times 4 \mu\)m aluminum square is deposited onto the remaining silicon island in the center so that there is a 1 \( \mu \)m margin around the perimeter of the pad. The island is completely suspended by the two PnC suspended structures attached on either side.

### 3. Results and Discussion

#### 3.1 Control of thermal conductivity by multiscale architecture

Following the Bose-Einstein distribution, the frequency distribution of phonons at room temperature can span from the MHz regime up to several THz. Among this spectrum, it is not clear which frequency band of phonons most contributes to thermal conductivity. If the aim is to reduce thermal conductivity for thermoelectric conversion material development, it is effective to introduce phonon scattering mechanisms that fit to the frequency distribution. Biswas et al. have reported a rapid improvement in ZT with efficient scattering of various phonon wavelengths over a wide frequency domain by creating three different scaled PbTe structures which they call an all-scale hierarchical structure\(^{22}\). Though we may also apply this approach for Si, since the distribution of thermal phonons in Si is quite different than in PbTe, we can follow a design based on the idea of a cumulative thermal conductivity. Figure 5 shows the cumulative thermal conductivity plotted against the distribution of thermal phonon MFP in Si at 300 K, which is calculated based on Debye-Klemens
The contribution to thermal conductivity by phonons is represented by the broken blue lines below. For example, phonons with MFP = 1 μm have a cumulative thermal conductivity of 0.5, but this means that half of the heat is being carried by phonons with a MFP of less than 1 μm. So, the thermal phonon density (broken lines) is mostly distributed in the region between 100 nm to 10 μm where the cumulative thermal conductivity (solid line) rises up drastically. This is the target region where introducing scattering mechanisms will be most effective. This relatively long and broad thermal phonon MFP range in Si at room temperature agrees with the calculations based on first-principles\textsuperscript{24}.

By PnC nanostructures, it is possible to scatter phonon modes in bulk with a MFP greater than 100 nm, but those with a MFP below 100 nm will remain largely unaffected. Consequently, when using polysilicon thin films with grain boundaries distributed in the 10’s of nm region, the belief is that this will enable the efficient scattering of thermal phonons with a short MFP. As a qualitative argument, based on the blue line representing MFP = 100 nm in Fig. 5, the wide range of thermal phonons distributed is considered to be covered in multiscale by the various scales of boundary scattering and surface scattering by PnC nanostructures.

Figure 6(a) shows the grain boundary distribution as obtained by analyzing TEM images of a non-doped Si surface grown by low pressure chemical vapor deposition system. As predicted, we were able to grow a polysilicon thin film with a grain size distribution spanning widely below 100 nm. By comparing the decrease in thermal conductivity by PnC nanostructures in both single crystal and polysilicon Si thin films, we can discuss whether or not the multiscale structures in silicon are effective. The thermal conductivity of PnC nanostructures with varying hole radii is shown in Fig. 6(b) for both single crystal and polysilicon thin films. The data for r = 0 nm corresponds to the thin film without holes. The thermal conductivity decreases as hole radius increases, but this is due to the drastic increase in occurrences of phonon surface scattering as the minimum distance between the inner walls of two adjacent holes, defined as the neck size (\(a - 2r\)), becomes narrow\textsuperscript{7}. Comparing the influence of PnC nanostructure patterning on thermal conductivity for \(r = 100\) nm with the values obtained for the thin film without holes, we observed a decrease from 75 Wm\(^{-1}\)K\(^{-1}\) to 38 Wm\(^{-1}\)K\(^{-1}\) for single crystal, and 10.5 Wm\(^{-1}\)K\(^{-1}\) to 4.3 Wm\(^{-1}\)K\(^{-1}\) for polysilicon structures\textsuperscript{21}. In Fig. 6(b), the thermal conductivity values for the thin film are clearly larger than the values obtained when extrapolating the values for PnC nanostructures from 50 nm to 0 nm. This discontinuous decrease in thermal conductivity is understood as the difference in phonon surface scattering. The surfaces causing phonon scattering in the membrane are parallel to the direction of thermal conductivity, but because the PnC nanostructures introduce holes with inner walls which are perpendicular to the direction of thermal conductivity, this is thought to be a result of strong backscattering. Also, for hole radii of \(r \geq 115\) nm, polysilicon Si showed a constant linear decrease while the single-crystalline Si showed a more drastic decrease in thermal conductivity as hole radius increased. Since the neck size becomes notably narrower compared to the 145 nm film thickness, it appears that the thermal conductivity in single-crystalline silicon is determined by neck size in this regime. On the other hand, since the boundary scattering at the interfaces of the polysilicon grain boundaries seem to determine the thermal conductivity, it is quite possible that a similar drastic increase may begin to appear if the neck size were to narrow even more.

In this paper, in order to limit the discussion to room temperature measurements with thermoelectric conversion applications in mind, though it is not plain to see the control of phonon transport based on the wave nature of phonons by the periodic structures that distinguish the field of phononics, it is possible to observe this phenomenon under sufficiently low temperature environments. Figure 4(b) shows results for the calculated phononic band diagram and heat flux spectrum in square lattice PnC nanostructures with a period of \(a = 300\) nm, and a hole radius of \(r = 135\) nm. The details of the simulation can be found in another work\textsuperscript{25}. The band diagram for our artificial periodic structure differs much from that of bulk silicon. Since the momentum \(k\) within the Brillouin zone provides a point of symmetry in small places, the band-folding effect occurs and multiple vibrational modes are being completely filled due to the finite geometry. With an appropriate design, it is possible to open a complete band gap near the frequency vicinity of the fundamental vibrational mode, where the modes have become sparse, and with our structure this exists near 10 GHz. The propagation has been completely prohibited for all phonons with frequencies within the band gap. A drop in the group velocity appears near the point of symmetry on the upper edge of the band gap, which is reflect-
ed in the heat flux. As shown in the right side of Fig. 4(b), we clearly observed lower heat flux in the PnC nanostructures as compared to the membrane without holes (gray line). Since the difference in heat flux becomes more significant at higher frequencies, we expect that it is possible to achieve a large decrease in thermal conductivity at high temperatures, but the shortening of the phonon MFP and thermal phonon wavelength due to more frequent incoherent scattering events induced by a temperature increase will actually weaken the fluctuation caused by sensitivity to surface roughness, and the band-folding effect will vanish. The concept of heat transport control based on the wave nature of phonons has been known for quite some time, however studying this phenomenon has always been a challenge due to the exceedingly difficult process of detecting the extremely small wavelengths of thermal phonons (around 1 nm at room temperature). Therefore, we do not think that the significant reduction of the thermal conductivities in PnCs shown in Fig. 6 stems from the wave nature of thermal phonons. In recent years, in low temperature environments in the range of 100 mK, there have been reports\(^{12}\) that suggest the possibility of making such observations, and in our research we continue to find success in tuning the thermal conductivity of silicon at 4 K by manipulating its crystallinity using PnC nanostructures.\(^{26}\)

### 3.2 Improvement of thermoelectric conversion by nanostructuring

While bulk silicon is typically not attractive as a thermoelectric conversion material, since it is widely abundant, offers a low environmental load and integrates well with existing microelectronics, there have been many attempts to develop silicon-based applications by dramatically improving its capability as a thermoelectric material through nanostructuring. Thermoelectric conversion characteristics have been reported in polysilicon thin films produced using MEMS and CMOS fabrication techniques.\(^{27–29}\)

The unitless Figure of Merit (ZT) of thermoelectric materials is expressed as \(S^2\sigma T/\kappa\), where \(S\) is the Seebeck coefficient, \(\sigma\) is the thermal conductivity, \(T\) is the temperature and \(\kappa\) is the thermal conductivity of the material. The thermoelectric efficiency \(\eta\) can be simply expressed in terms of ZT:

\[
\eta = \frac{T_H - T_C}{T_H} \cdot \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_C/T_H}
\]

Here, \(T_H\) is the temperature of the high temperature source, \(T_C\) is the temperature of the low temperature source, and \(T\) is the average temperature. The first term is the Carnot efficiency which determines the upper limit. We have seen a number of works in the past few decades using a variety of material systems and structures which employ electrical enhancements that aim to increase the power factor \(S^2\sigma\) by considering molecular structure and density of states near the Fermi surface, as well as structural enhancements which aim to decrease lattice thermal conductivity by phonon transport control, as an approach to realize a large ZT value. There also appear to be a large number of comprehensive explanations concerning the design guidelines of high efficiency thermoelectric conversion materials at the nanoscale.\(^{30}\)

By patterning the PnC nanostructures on the doped polysilicon membrane, we were able to determine the degree of possible improvement in our device. Figure 7(a–d) shows the profiles and SEM images of 2D PnC nanostructures which were fabricated in order to make both electrical and thermal conductivity measurements. Boron and phosphorous were used as the p-type and n-type dopants at carrier concentrations of approximately \(2 \times 10^{20}\) cm\(^{-3}\) and \(8 \times 10^{20}\) cm\(^{-3}\), and film thicknesses of 149 nm and 145 nm respectively. The details of the growth conditions are explained in Ref. 31. Samples used for measuring electrical properties have 2D PnC nanostructures grown on SiO\(_2\) and Al electrical contacts evaporated onto the structure to allow for four terminal electrical measurements. The profile of this structure is shown in Fig. 7(b). Samples used for measuring thermal properties have the same construction as described above.

Both electrical and thermal conductivity for p-type and n-type nano polysilicon 2D PnC nanostructures were acquired using the four terminal technique and micro-thermoreflectance technique, and these results are shown in Fig. 8. Similar to thermal conductivity, electrical conductivity also shows a tendency to decrease as the hole radius increases, but unlike thermal conductivity the rate of decrease appears to be much slower and shows no discontinuous decrease from the values for the membrane. This is due to the influence of surface scattering by PnC nanostructure and the fact that the MFP of electric charge carriers is one order of magnitude shorter than that of a phonon. The Seebeck coefficients used in calculating ZT for the results shown in Fig. 8(c) for p-type and n-type samples were \(240 \mu V/K\) and \(-81 \mu V/K\) respectively.\(^{30}\) It is clear that the value of ZT rises along with the increase in hole radius, and when \(r = 110\) nm the ZT value for the p-type sample increased approximately 2 times, and n-type approximately 4 times, compared to the bulk membrane. This indicates that the dimensions of our structure emphasize the difference in MFP between electric charge carriers and phonons as a result of the remarkable decrease in thermal conductivity compared to the change in electrical conductivity. By narrowing the neck width we might expect a further rise in the ZT value, but due to the increase in electrical resistance at hole radii \(r > 140\) nm, in the region where the MFPs of electric charge carriers and phonons are comparable, there may exist an optimum hole diameter.
Thermoelectric conversion devices are often used by placing the object against various surfaces with differing temperatures, so electric current and heat flux is made to flow vertically along this surface. However, the structures we have introduced were constructed so that the electric current and heat flux flow in-plane, so this aspect of the device will need to be assessed in future designs. Until now, electrical power per unit area on the range of 1 μWcm⁻² with a 10 K temperature difference has been reported using CMOS and MEMS technology to fabricate structures that can produce a temperature difference along the in-plane direction. As shown in Fig. 1(a), at 900 K silicon demonstrates the highest performance compared to other materials. At room temperature, silicon devices perform at only 10% of this level, which is relatively low when compared to materials such as BiTe which exhibit very high performance at room temperature.

However, when considering energy harvesting applications which are needed to build the wireless network that will contribute to a smart society, it is enough to drive the microsensors and when combined with a capacitor could potentially operate several times in one day which is sufficient for a variety of uses. A device that can output 1 μWcm⁻² will be able to fulfill this energy requirement and since it is cheap and has a low environmental load, silicon can be considered as one possible choice for thermoelectric conversion material development.

4. Conclusion

Since the 1990’s, improvements in nanostructure forming technology have taken thermoelectric conversion material development in a new direction. Since heat transport in nanostructures is a complex issue, even today many phenomena remain unclear and we hope to see development in this field in the near future. Certainly, if achievable, the development of a thermoelectric conversion material with both a high conversion efficiency and low environmental load will contribute to solving the current energy issues and building a smart society. In this paper, we have investigated the physics of thermal conductivity in polysilicon PnC nanostructures and its conversion characteristics in order to evaluate such a device as an approach to these modern day issues. We have shown that in order to effectively control thermal transport it is important to have control over thermal phonons dispersed over a large area, and we also demonstrated that an improvement in the ZT value of polysilicon by three times that of bulk material is possible through PnC nanostructuring and multiscale layered structures with various scale phonon scattering mechanisms.

Acknowledgements

The contents of this work were obtained by the research activity with Jeremie Maire, Yuta Kage, Roman Anufriev at the University of Tokyo, and Oliver Paul and Dominik Moser at Freiburg University. The author acknowledge Kazuhiko Hirakawa and Junichiro Shiomi for fruitful discussion, and Yasuhiro Arakawa for technical support. This work was supported by the Project for Developing Innovation Systems of MEXT, Japan, by KAKENHI (25709090).

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