ELECTRICAL AND THERMAL TRANSPORT IN 2- AND 3-DIMENSIONAL PERIODIC HOLEY SILICON

BY

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DISSERTATION

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Silicon, one of the most abundant elements on earth, is a promising candidate for thermoelectric applications in the form of different nanostructures. It has been conclusively demonstrated that boundary scattering in nanostructured silicon effectively reduces thermal transport, resulting in an enhanced thermoelectric figure of merit $ZT$. However, claims of high $ZT$ are quantitatively misleading since electrical and thermal properties are often characterized on separate samples due to measurement complexity. In the first part of this dissertation, we design, fabricate and employ a novel integrated microdevice to measure all three thermoelectric properties of 2D holey-silicon thin films. We systematically vary doping across samples using diffusion doping over a barrier layer. While the size of the sample has minimal impact on electrical conductivity, we find the Seebeck coefficient (and hence, the power factor) to be substantially suppressed. By examining the temperature trend and comparing with available bulk data, we find the reduction to be explained through quenched phonon drag resulting from phonon boundary scattering. The thermal conductivity of these samples remain relatively in agreement with the Casimir limit. The total increase of $ZT$ is $\sim 4$ times when compared against bulk silicon at 300 K. The second part of this dissertation measures the temperature dependent thermal conductivity of 3D periodic silicon inverse opals. Beside the anticipated low thermal conductivity due to high porosity, we observed an anomalous $\sim T^{1.8}$ dependence at low temperatures, distinct from the typical $\sim T^3$ behavior of bulk polycrystalline silicon. Using phonon scattering theory, we show such dependence arising from coherent phonon scattering in the intergrain region. This unique observation of coherence effect at grain boundary may be attributed to a thinner intergrain region formed when intragrain growth is limited by shell thickness during prolonged annealing. This work provides insight into coupled charge
and heat transport in silicon nanostructure with periodic holes in 2- and 3-dimensions.
To my wife, Shenglan
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CHAPTER 1

INTRODUCTION

1.1 Motivation and Background

Each year, according to the Department of Energy [1], about 60% of the total energy generated in United States is rejected as waste heat. In 2014, that number is 59.4 Quads, equivalent to $17.6 \times 10^{12}$ kWh. Though not all energy could be recovered according to principles of thermodynamics, the amount of exergy is still huge. Most of the dumped heat is between 40°C and 250°C, and if we assume the average heat source temperature is 150°C, the maximum efficiency we can achieve is $\sim 30\%$ using a Carnot engine. A practical cycle will of course operate at a much lower efficiency, but this waste heat recovery process is still very attractive given the massive amount available. However, most conventional fluid machines are not built for such low temperatures. Others using trans-critical CO$_2$, organic Rankine or Kalina cycle are cost-ineffective to operate and possess humongous engineering complexity. Amongst a handful options, solid state energy conversion using thermoelectrics has some distinctive advantages. It exploits the Seebeck effect, which produces a voltage bias from a temperature gradient, as power source. A thermoelectric module is usually made of a $\pi$-junction as shown in Figure 1.1a, in which p-type and n-type materials are connected thermally in parallel and electrical in series. In this way, as heat is dissipated from hot to cold side, electrical current flows from the n-type material to p-type material. As a result, an open circuit voltage is established between the two legs. Microscopically, Seebeck coefficient may be seen as the ratio of two fundamental quantities a charge carrier can transport: energy and charge ($k_B/e$, where $k_B$ is Boltzmann constant and $e$ is fundamental charge). The magnitude is usually very small ($\sim 0.1$ mV/K), therefore many of the $\pi$-junctions are
Figure 1.1: Thermoelectric module illustration and $ZT$ impact to overall energy conversion efficiency. Left: Schematic of a $\pi$-junction showing p-type and n-type materials are connected thermally in parallel and electrical in series. Both holes and electrons travel from hot to cold side, forming an open circuit voltage. Right: The thermoelectric efficiency, depicted as fraction of Carnot, is plotted against material $ZT$. If the heat source and sink temperatures are at 150°C and 27°C respectively, the overall conversion efficiency is $\sim$4% for $ZT = 1$.

The efficiency of such a device relies heavily on the materials. The thermoelectric figure of merit $ZT$ is often used to quantify the goodness of a material. It is defined as $ZT = (S^2\sigma/k)T$, where $S$ is the Seebeck coefficient, $\sigma$ and $k$ are the electrical and thermal conductivity, and $T$ is the average operation temperature in absolute scale (Kelvin). Figure 1.1b shows the fraction of Carnot efficiency given $ZT$ of a material. If the heat source and sink temperatures are at 150°C and 27°C respectively, the overall conversion efficiency is $\sim$4% for $ZT = 1$. The challenge in field of thermoelectrics is to find a scalable material with good $ZT$. The benchmark is Bi$_2$Te$_3$, which has a $ZT$ of roughly 1 at room temperature. However, this rare earth material is too expensive to scale up.

On the other hand, silicon’s economy of scale and compatibility with current IC fabrication process make it extremely appealing for thermoelectric application. However, even though its power factor $S^2\sigma$ ($3.2 \times 10^{-3}$ W/mK$^2$) is as good as Bi$_2$Te$_3$, single crystalline silicon was not traditionally considered to be a good thermoelectric material due to its high lattice thermal conductivity. For bulk silicon, thermal conductivity is 148 W/mK at 300
K and $ZT$ is roughly 0.01 [3] even at the optimal doping condition. Recent studies [4–14] have shown that it is possible to enhance $ZT$ in silicon nanostructures by reducing thermal conductivity. At 300 K, mean free paths (MFPs) of conducting phonon in bulk silicon span 3 orders of magnitude from less than 10 nm to several micrometers. Phonon with MFP more than 100 nm contributes more than 3 quarters of the total conductivity as shown in Figure 1.2 from first principle calculation [2]. Intentionally suppress long MFP phonon transport, by introducing more scattering events, could drastically reduce the lattice thermal conductivity. The most common way is to exploit boundary scattering in nanostructures. While most of the studies emphasizes on the reduction in thermal conductivity, effect of boundary scattering on electrical conductivity and Seebeck coefficient is explored to a relatively less extend. In fact, there is no single experiment show conclusively how $k$, $\sigma$ and $S$ would change in silicon nanostructure.
1.2 Phonon and Electron Transport in Silicon Nanostructures

1.2.1 Thermal conductivity

In silicon, lattice phonons dominate heat transport. The electronic thermal conductivity is less than 0.5% of the total $k$ even at $1 \times 10^{19}$ cm$^{-3}$ carrier concentration. Phonon is the quantization of lattice vibrations. As a quasi-particle in quantum mechanics, its contribution to conduction can be viewed as analogs of a gas system. From kinetic theory [15], lattice thermal conductivity is

$$k = \frac{1}{3} \sum_{j, \omega} C_v \Lambda,$$

where $C$, $v$ and $\Lambda$ are frequency dependent phonon heat capacity, velocity and MFP respectively, $\omega$ and $j$ are the angular frequency and polarization of phonon mode. In silicon nanostructures with limiting dimension $> 20$ nm, the phonon dispersion relation is almost identical to bulk [16]. Therefore, we don’t expect changes in $C$ and $v$. However, phonon MFP is now dominated by boundary scattering. Casimir limit [17] of thermal conductivity assumes completely diffuse boundary scattering and the resulting phonon MFP is similar to the limiting dimension of nanostructure. Reduction in thermal conductivity in nanostructures has been demonstrated experimentally in the form of nanowires [4–6], holey thin film [7–12] and 3D periodic silicon [13]. In Figure 1.3, we plot those experimental data against limiting dimensions at 300 K. The corresponding Casimir limit is also plotted for comparison. We note that for larger nanostructures, the data follows Casimir limit down to $\sim 200$ nm. However, $k$ for structures with limiting dimension $< 200$ nm falls significantly below the Casimir limit. It is not clear at present whether this discrepancy has origins in the measurements themselves. Fabrication of features at the smaller end is clearly challenging and the presence of subtle defects such as at the boundaries is difficult to detect as well as rule out. Various attempts [18–21] seek to explain the small conductivity below Casimir limit including wave-like coherence effect, but a consistent theory is lacking. A lot of puzzles still remain.
Figure 1.3: Summary of room temperature intrinsic material thermal conductivity data of nanowires (solid symbol) and holey thin films (open symbol) plotted against the limiting dimension for surface scattering. The corresponding Casimir limit is shown for comparison.

One way to examine the crystal quality of silicon nanostructure is to measure the electrical property. Silicon nanostructure with less defects should possess similar electron mobility as bulk. In addition, measuring both electrical and thermal conductivity cancels the porosity effect on $ZT$. Unfortunately, existing data that shows unusual small thermal conductivity seldom reports electrical measurement. Even for those with reported $ZT$ [5, 10], measurement was not done strictly on the same sample. A recent measurement [12] showing thermal conductivity below Casimir limit also reveals inferior electrical conductivity.

1.2.2 Electrical conductivity

Charge transport in silicon has been extensively studied in 1980s [22, 23]. In this section, we will summarize the understanding in bulk silicon, and extend it to silicon nanostructures.

Carrier mobility can be expressed using the Kubo-Greenwood formula
\[ \mu = \frac{2e}{3n} \int_0^\infty D(E)E\tau(E)m_c^{-1} \left( \frac{\partial f_0}{\partial E_F} \right) dE, \]  

(1.2)

where \( n = \int_0^\infty D(E)f_0(E)dE \) is the electron density, \( D(E), \tau(E), f_0 \) and \( m_c \) are density of states, energy dependent relaxation time, Fermi distribution and conductivity mass respectively. For bulk n-type silicon, those expressions are readily available from aforementioned literature. However, to fully understand the size effect, we need to compute the background electron relaxation time with respect to carrier concentrations.

Assuming all scattering events are independent, we can use the Matthiessen’s rule to obtain the background relaxation rate, which is related to individual relaxation rates as

\[ \tau^{-1} = \sum \tau_i^{-1}, \]

where \( i \) represents phonon, impurity, electron-electron, and plasmon scattering. We use deformation potentials [22] to model intra-valley and inter-valley phonon scattering. Following Fischetti [23], we use the Brooks-Herring formula [24] to compute the relaxation time due to ionic impurities. We account for phase shift [25] at doping levels greater than \( 10^{17} \text{ cm}^{-3} \) to correct the Born approximation in the Brooks-Herring formula. Electron-electron scattering does not affect mobility directly, as momentum is transferred between electrons. This, however, modifies the energy distribution and is accounted for in our calculations [25]. Finally, we follow Fischetti [23] in the treatment of plasmon scattering. Figure 1.4 plots different scattering rates as a function of the electron energy. We include a simplistic boundary scattering rate, \( \tau_b^{-1} = v/d \) here for comparison. The figure plots ionic impurity and plasma scattering rates at two different impurity concentrations to illustrate their dependence of doping.

As shown in Figure 1.4, electrons scatter more against ionic impurities and plasma for increasing doping. At \( 10^{19} \text{ cm}^{-3} \), the dominant mechanisms are ionic impurity and plasma scattering for most conducting electrons. For limiting dimension of 100 nm, the scattering rate is shadowed under acoustic and inter-valley scattering. Essentially, this means even for lightly doped silicon sample, the effect from boundary scattering is not significant. On the other hand, when limiting dimension reduces to 25 nm, boundary scattering is now at the same level of electron-phonon scattering. In lightly doped silicon, a reduction in mobility is substantial. However, this reduction is attenuated when doping-dependent scattering processes start to dominate.
Figure 1.4: Scattering rates of electrons for different processes in silicon at 300 K. Solid lines represent scattering mechanisms insensitive to doping. Dashed and dot-dashed lines represent doping levels of $10^{17}$ cm$^{-3}$ and $10^{19}$ cm$^{-3}$ respectively. Boundary scattering from two limiting dimensions (25 nm and 100 nm) are shown.

At $10^{19}$ cm$^{-3}$, boundary scattering is again insignificant.

To illustrate the effect of boundary scattering, we calculated mobility in silicon at 300 K for different doping levels. In this calculation, we used Eq. 1.2 and all the energy dependent scattering rates. Together with bulk data [26, 27], the calculations are plotted in Figure 1.5. Black and blue curves represent mobility for bulk silicon and silicon nanostructure with limiting dimension of 25 nm. Their relative magnitude echoes the discussion in scattering rates: even at 25 nm, boundary scattering poses an insignificant effect at higher doping levels. In fact, the reduction in mobility is less than 10%. If the limiting dimension is increased from 25 nm to 100 nm, mobility remains virtually the same as in bulk.

From the perspective of mean free path, dominant conducting electrons have MFPs less than 10 nm. If we average it over electron energy and density of states, the number is about 3 nm for doped silicon at $10^{19}$ cm$^{-3}$. As a result, adding a scattering event with MFP $\sim$25 nm is just unimportant. Needless to say for 100 nm.
Figure 1.5: Electron mobility in silicon at 300 K for different doping levels. Black and blue curves represent calculations for bulk silicon and silicon nanostructure with limiting dimension of 25 nm. The bulk data are from Ref. [26] (open circles) and Ref. [27] (crosses).

Having said all of the above, making a nanostructure with limiting dimension of 25 nm in reality is still challenging. The presence of defects, surface roughness or disorder could all depreciate electrical conductivity. At the same time, those additional scatters may also be responsible for thermal conductivity below Casimir limit. Therefore, it is extremely important to measure electrical and thermal conductivity on the same sample.

1.2.3 Seebeck coefficient

Seebeck coefficient is the open circuit voltage of a thermoelectric material for a unit temperature difference. Its importance in $ZT$ is amplified by the quadratic dependence. The power factor $S^2\sigma$ is often used to characterize the electrical part of thermoelectrics. Seebeck coefficient in silicon arises from two contributions: diffusion part and phonon drag. The diffusion contribution is the average energy transported by carriers with respect to Fermi level:

$$S_d = \frac{1}{eT} \left< E - E_F \right>.$$  \hspace{1cm} (1.3)
In n-type semiconductor, when Fermi level is under or above but close to conduction band, $S_d$ is large due to strong asymmetry of density of states around Fermi level. This corresponds to lightly/moderately doped silicon. When Fermi level is moved up, this asymmetry gradually diminishes and $S_d$ is consequently reduced. The general trend of this diffusion component is decreasing for increasing doping. Some attempts in increasing $S_d$ have been made through band structure engineering in low dimensional structures [28–30]. Specifically, researchers modified the density of states around the Fermi level such that a greater asymmetry is achieved. However, the dimensions applied in those studies are out of the scope of this dissertation.

Since $\sigma$ increases with doping, there is a trade off to maximize $S^2\sigma$. The optimal doping concentration is $\sim 10^{19} - 10^{20} \text{ cm}^{-3}$ in silicon [3,31].

The phonon drag part $S_{ph}$ arises due to momentum transfer from long wavelength phonons to electrons, which 'drags' electrons from hot towards cold side. The resulted voltage polarity is the same as diffusion part therefore total Seebeck voltage is the combination of these two. Compared with its diffusion counterpart, phonon drag is relatively less understood and a formal theory with strong experimental evidence is lacking. The difficulty in obtaining an accurate expression is partly due to the seemingly impossible separation between two contributions and the lack of a systematic study with controlled variables like: temperature, doping level and structure size. Some controversy in experimental data [6,32] also confuses the whole picture, therefore more measurement is needed.

In general, phonon drag is dominant at low temperature where long wavelength phonons also have long MFPs. These phonons are able to transfer the momentum to electron before they get randomized by a scattering event. As temperature increases, Umklapp scattering becomes significant and the drag component is therefore reduced. On the other hand, the transferred momentum also gets lost through scattering processes like ionic impurity and plasma scattering as doping increases. This attenuation is analogous to the reduction in electron mobility we discussed earlier. Adding boundary scattering into the picture also changes $S_{ph}$ because phonon population has been modified. Reports have shown the $S_{ph}$ increases due to stronger coupling between phonons and carriers [6]. However, in a recent published article [32],
we observed completely quenched $S_{ph}$ in silicon nanowire possibly due to reduced MFPs of long wavelength phonons.

For thermoelectric applications (doping $\sim 10^{19} - 10^{20}$, $T > 300$ K ), it is generally accepted that drag component is much smaller than diffusion part [33], and alternations in $S_{ph}$ in nanostructure are often not considered. Whether to neglect $S_{ph}$ in doping and temperature range mentioned above is still debatable as new evidences [32] show $S_{ph}$ in bulk is still substantial. Estimating $S_{ph}$ contribution is another objective of this dissertation.

1.3 Thesis Structure

The remaining chapters in this dissertation is structured as follows.

In Chapter 2, we review and discuss the existing theories and experimental results on the transport phenomena in periodic nanostructures, mostly silicon. Specifically, in Section 2.1 we first examine models that describe transport properties in continuum and sub-continuum regime, as well as a random walk approach in periodic structure. Then in Section 2.2 we compare experimental data in the literature with the models, and analyze the current understanding of thermal transport in such structures. A substantial portion of this chapter is dedicated to the debate between coherent and incoherent phonon scattering, which are proposed to explain thermal conductivity below Casimir limit.

In Chapter 3, we used a micro-fabricated device to measure all three thermoelectric properties on 2D holey silicon. We discuss in detail the fabrication process and measurement principles. Thermoelectric properties are reported for different doping and porosity levels. We discuss the cause of discrepancy with bulk values. In addition, we also present $ZT$ values with temperature and estimate $S_{ph}$.

In Chapter 4, we present our measurement of silicon inverse opal, which is an extremely porous material. We show our fabrication process and measurement technique. The effective thermal conductivity is $\sim 1$ W/mK, same order of magnitude as silicon dioxide. Interestingly, we observed an unusual
temperature dependence of material thermal conductivity at low temperature which we attribute to a novel coherent scattering process between long wavelength phonons and grain boundaries.

Chapter 5 summarizes the contribution of this dissertation and points to the direction of future research.
CHAPTER 2

TRANSPORT PHENOMENA IN HOLEY NANO-STRUCTURE

2.1 Modeling Approaches for Periodic Holey Structures

In this section, we discuss different levels of theory for considering thermal transport in periodic holey structures, starting from continuum heat diffusion and culminating in sub-continuum incoherent and coherent transport of phonons respectively. Combined with experimental data and our calculation (and simulation), this discussion advances the understanding of phonon transport in periodic porous structure spanning from meso- to nanoscale.

2.1.1 Continuum Considerations

Transport properties in a multiphase system can be very different from that of each of the constituents. There are several models to describe the relationship between effective properties and intrinsic properties of each material, among which the simplest are the parallel and series resistance network models [34]. These yield the theoretical upper and lower bounds on effective transport properties respectively. They apply to the ideal situation where the two materials are stacked on each other and the direction of transport is either parallel or perpendicular to the material. If the conductivities of the two materials are $k_1$ and $k_2$ ($k_1 > k_2$), the effective conductivities given by each model are

\[ k_{\text{parallel}} = \frac{k_1 + k_2}{2} \]
\[ k_{\text{series}} = \frac{k_1 k_2}{k_1 + k_2} \]

---

\[ k_{\text{eff}} = (1 - \phi)k_1 + \phi k_2 \]  
\[ k_{\text{eff}} = \left[ \frac{1 - \phi}{k_1} + \frac{\phi}{k_2} \right]^{-1} \]

respectively, where \( \phi \) is the volume fraction of the second material. In practice, the model is not physically realistic for porous structure (i.e. one “material” is air or vacuum) and the bounds are quite far apart to make reasonable estimations.

A more realistic and narrower bound approach is the geometry-independent Hashin and Shtrikman model [35], which applies to one material embedded into a continuous host material. The upper and lower bounds of the effective conductivity are

\[ k_{\text{eff}}^u = k_1 + \frac{3\phi k_1(k_2 - k_1)}{3k_1 + (k_2 - k_1)(1 - \phi)} \]

\[ k_{\text{eff}}^l = k_2 + \frac{3(1 - \phi)k_2(k_1 - k_2)}{3k_2 + (k_1 - k_2)\phi} \]

This model works well if the contrast between \( k_1 \) and \( k_2 \) is not large. For instance, if the ratio \( r = k_2/k_1 \) is 0.2, taking the geometric mean of the upper and lower bounds gives a reasonable estimation with maximum uncertainty of 11%. However, for a porous system where the second phase is air or vacuum, the lower bound becomes zero and remains far apart from the upper bound. The geometric mean is therefore not an accurate estimation of the effective conductivity in this case.

The well-known effective medium theory (EMT), originally proposed by Maxwell [36], takes better account of geometric effects. In the model, the temperature field perturbation due to many small inclusions is thought to be the same as one big inclusion, for which the effective conductivity is then calculated. The shape of the imbedded material is generalized as a spheroid and \( \alpha \) is the ratio between the length of unequal axis and that of one of the equal axes. It is found that a system with sphere inclusions (\( \alpha = 1 \)) represents the upper limit of the H-S model. If these inclusions are voids, the H-S model
reduces to the well-known Maxwell-Garnett (MG) model

\[ k_{\text{eff}} = \frac{(1 - \phi)k_0}{1 + \phi/2}, \]  

(2.5)

where \( k_0 \) is the conductivity of the host medium. When the inclusions are thin-disk like \((\alpha \to 0)\), the EMT predicts that the effective conductivity is the lowest and coincides with the lower bound of the H-S model. Another special case applies to a 2D system with infinitely long cylindrical voids where

\[ k_{\text{eff}} = \frac{(1 - \phi)k_0}{1 + \phi}, \]  

(2.6)

which lies in between aforementioned bounds. Therefore EMT does not narrow the bounds by H-S model, but provides a more accurate estimation if the shape of the inclusions is available. Predictions from the linear model and the two MG models for a porous structure are shown in Figure 2.1.

In general, EMT provides a good estimate at small \( \phi \) or when the contrast between the two materials is small. However, the prediction for a system with large porosity and/or big contrast between materials is not reliable. A more intensive but accurate approach is to solve the heat diffusion equation to obtain the effective conductivity for a specific periodic structure. Albrecht et al. [37] have formulated a boundary-integral method for calculating the conductivity of structures with two- and three-dimensional periodic lattices.

Figure 2.1 also shows the effective conductivities of a 2D square lattice with cylindrical voids, an opal [38] and an inverse opal [39] structure respectively. Unsurprisingly, the curve for the 2D square lattice agrees well with the MG model for \( \alpha \) as large as 0.5. Beyond this, it deviates sharply until it finally tends to 0 at \( \alpha = 0.785 \), at which porosity the system becomes discontinuous. The behavior is different in an opal structure, which is an FCC array of overlapping spheres. When \( \alpha \) is smaller than 0.1, the conductivity approximately follows the MG model. However, for increasing \( \alpha \), the overlapping volume between adjacent spheres becomes smaller, creating a bottleneck effect. The conductivity goes to zero when \( \alpha = 0.26 \), at which the spheres disconnect from each other.
Figure 2.1: The porosity effect on thermal conductivity from different continuum models including the notable effective medium models. The calculations by boundary-integral method for FCC opal, 2D square lattice (cylindrical voids) and inverse opal are shown for comparison.

Another interesting structure is an inverse opal, which can be made by filling the pores inside an opal structure followed by removal of the original opal template. It is a highly porous structure as the to-be-removed opal template occupies 74% of the volume. Surprisingly, the trend for the conductivity of an inverse opal is very similar to the predictions of the MG model. In fact, the prediction by the MG model overestimates the exact solution by only 10% for the realistic porosity range. The accuracy results from the fact that an inverse opal is effectively a thin film network, where all of the material comprising the inverse opal contributes similarly to the resistance. In contrast, in an opal structure, the dominating resistance arises in the overlapping portions of spheres and the remainder of the material has markedly lesser contribution to the resistance [40].

2.1.2 Random Walk in Periodic Structures

While an effective thermal conductivity can be readily estimated from measurements through use of results from continuum theory as discussed previ-
ously, it is not clear at what feature size this approach is no longer justified. Sofo and Mahan [40] have considered the problem of a classical particle diffusing inside a periodic structure when the mean free path is still smaller than the period but within an order of magnitude. By integrating out random walks inside individual blocks and instead focusing on diffusion from block to block through the interconnecting necks, they elegantly reduced the problem to diffusion in a lattice but with residence time at each site. In this manner, they derived diffusion coefficients for 1-D, 2-D and 3-D periodic structures. For a random walk in 3-D, it is well known that the diffusion coefficient, $D_o$ in the bulk is related to average speed of the particle, $v$ and its mean free path, $\Lambda$ as $D_o = 1/6v\Lambda$. Sofo and Mahan show that the coefficient $1/6$ appearing in this relation is reduced by 50% in a face-centered cubic opal when the diameter of the characteristic sphere is a few times (<10) the mean free path. This implies that even for phonon modes with mean free paths smaller than the feature size, we may expect a reduction in effective transport. When the mean free path is comparable to the feature size, sub-continuum rather than continuum transport is expected to play a significant role. This is discussed in the next section.

2.1.3 Sub-continuum Phonon Transport

The discussion so far has implicitly assumed that feature sizes are much larger than the phonon mean free paths. As mentioned in Chapter 1, phonon mean free paths larger than 1 $\mu$m contribute significantly to heat conduction. [2, 41, 42] In structures with sub-micrometer feature sizes (film thickness and/or pitch of holes), phonon transport will be modified from the bulk. Clearly, at a small enough feature size, the distribution function for phonons transporting heat in the structure would depend on the specific geometry of the structure and would not be the same as in the bulk. The most detailed consideration of transport in periodic structures till date involves modeling phonons through either atomistic simulations [21, 43, 44] or tracking their trajectories through Monte Carlo simulations [19, 45]. We review basic phonon scattering physics in this section.

Phonons in a periodic structure will be scattered at the boundaries of the
crystal and if present, at grain boundaries, by other phonons and from impurities. For bulk silicon at room temperature, the phonon MFP is dominated by three-phonon Umklapp scattering. The surface boundary scattering is relatively more influential at low temperature, where three-phonon processes are substantially suppressed. The Casimir model [17] for boundary scattering assumes complete thermalization of incident phonons at the boundaries of a crystal to predict MFP comparable to the crystal dimensions. It is illustrative to consider rates associated with various phonon scattering mechanisms. Scattering rate available in the literature [46, 47] for Umklapp scattering is of the form $\tau_u^{-1} = BT\omega^2e^{-C/T}$. The values of $B$, $C$ can be determined by recursively fitting the high temperature thermal conductivities of bulk silicon and nanostructures, and are found to be $B = 1.6 \times 10^{19}$ s/K, $C = 152$ K. Using Casimir’s approach, the boundary scattering rate is $\tau_b^{-1} = v/(Fd)$, where $v$ is the phonon speed, $F$ is a geometric factor, and $d$ is the characteristic dimension. Mass difference (isotope) scattering can be obtained from $\tau_m^{-1} = V_0\Gamma/(4\pi v_s^3)\omega^4$, where $v_s$ is sound velocity, $V_0$ is the volume per atom, and $\Gamma$ is defined as $\Gamma = \sum_j f_j(1 - M_j/M)^2$. Here, $f_j$ is the percentage of atom type $j$, whose mass is $M_j$, and $\bar{M}$ is the average atomic mass. The effect of both isotope and impurity scattering can be evaluated using this equation. For isotope scattering in silicon, it is commonly taken $V_0\Gamma/(4\pi v_s^3) = 1.32 \times 10^{-45}$ s$^3$.

In polycrystalline silicon, grain boundary scattering is usually treated as a frequency independent process, in which the grain size is the limiting dimension [48]. However, recent measurements show that the scattering process due to grain boundary is a rather complicated mechanism [13,49]. Different approaches have been proposed to fit the corresponding measurement values. One of those argues that phonons with longer wavelength scatter coherently with thinner grain boundary [50]:

$$\tau_g^{-1} = \frac{3\omega^2l^2}{4v}(\Delta v/v)^2,$$  \hspace{1cm} (2.7)

where $t$ is the thickness of intergrain region, $l$ is the average grain size, $\Delta v$ is the change in velocity at the boundary. The origin of this scattering process will be explained in Chapter 4.

In Figure 2.2 all the empirical scattering rates are plotted as a function
Figure 2.2: Frequency dependent phonon scattering rates calculated for silicon. Rates for Umklapp scattering are shown at 30 and 300 K. The characteristic dimension for both surface and grain boundary scattering is 100 nm.

of frequency. To address the effect of temperature, Umklapp scattering is plotted at 30 K and 300 K. We use $d = l = 100$ nm for both surface and grain boundary scattering. Overall, surface scattering dominates at low frequencies and grain boundary scattering dominates at higher frequencies. The contribution from grain boundary scattering is always significant except for very low frequencies. Note that Umklapp scattering rates are always smaller than the dominant rates for feature size at 100 nm, even at 300 K.

Consideration of phonon transport in periodically porous nanostructures is complicated due to geometry. First attempts in this direction [51–53] simplified the treatment of phonon scattering while focusing on solving the Boltzmann equation in the challenging geometry. The main conclusion from these studies was that sub-continuum transport is indeed an important factor to consider in evaluating thermal conductivity of these structures. Atomistic simulations [21,43,44] provided more insight into the role of various phonon scattering mechanisms, particularly surface scattering, and suggested that it was possible to obtain thermal conductivity close to the amorphous limit with truly nanoscale features. More recent theory [19, 45], following the
publication of data on nanostructures, has revisited the Boltzmann transport simulations while considering frequency dependent scattering rates. These are discussed further in Section 2.2.

2.1.4 Coherent Phonon Transport

Coherent phonon transport refers to the condition where the relative phase of phonons plays a role in the transport process typically introducing wave effects such as interference or localization [54]. While similar transport has been investigated extensively in the case of electrons [55] and photons [56], only a relatively small amount of work has focused on phonons, notably in core-shell nanowires [57–59]. An important concept in describing coherent transport of energy is the coherence length, $L_c$. This concept has origins in optics where the coherence of a light beam is related to the coherence in the source. In the framework of quantum mechanics, the simplest interpretation of coherence length for a quantum particle is that $L_c$ is the spatial spread of the wave packet representative of the particle; its estimation, however, differs between different particles and between different prevalent scattering mechanisms. For example for electrons in a metal, $L_c$ is typically the product of the Fermi velocity and the phase relaxation time. The phase relaxation time is typically shorter than the momentum relaxation time that defines the electron mean free path. However, it is possible to have situations where the phase relaxation time exceeds the momentum relaxation time i.e. the phase is conserved over several collisions even as the direction of momentum is randomized. In this case the coherence length is related to the diffusivity of the electron.

In the case of photons, one interpretation is that $L_c \sim c/\Delta\omega$ where $c$ is the speed of light and $\Delta\omega$ is the bandwidth of waves. A ray of electromagnetic waves comprising a stream of photons is a series of wave packets emitted from individual emitters at the source. Each wave packet then has a coherence length and can interfere with itself. For (incoherent) thermal radiation, the effective bandwidth arises from the Heisenberg uncertainty relation as the energy spread $k_BT$ divided by the Planck constant, $\hbar$. This bandwidth is $6$ THz at room temperature. Replacing the speed of light with the speed of
sound, $v_s$, the coherence length for thermal phonons is then $L_c \sim v_s h/k_B T$. When estimated in this approximate manner, $L_c < 10$ Å at room temperature. Recent calculations [60] of the frequency dependent coherence length for phonons in silicon consider coherence to be the spatial correlation of the atomic displacement fluctuations at equilibrium. Using the Stillinger-Weber potential, the calculated coherence lengths are larger than the figure for $L_c$ from above and can be as high as several tens of nanometers for THz frequency phonons.

There is considerable debate on the role played by coherence. The effect may be any combination of opening of band gaps, alteration in the density of states, reduction of group velocities or localization of modes. Significant band gaps are necessary in the THz frequencies to affect thermal transport and it is unlikely that current feature size of 100 nm or larger are sufficient at creating such gaps. Change in density of states and a reduction in phonon velocities is also much debated. We further discuss transport theory related to coherence in Section 2.2.

2.2 Literature Review and Discussion for 2- and 3-D Periodic Structures

In this section, we discuss experimental results for thermal transport in 2-D and 3-D periodic holey nanostructures in the literature. We start with the methods for fabrication as well as the measurement techniques and finally summarize key data reported till date.

2.2.1 Two-Dimensional Structures

In this subsection we present an overview of the methods reported for fabricating 2-D periodic holey silicon [7–10, 12, 61] and discuss techniques used in measuring thermal conductivity. In the first experimental work on thermal transport in periodic silicon structures, Song et al. [7] used a silicon-on-insulator (SOI) wafer to fabricate a silicon membrane resting on buried silicon oxide. The top surface was coated with Si$_3$N$_4$ prior to membrane preparation.
and the buried oxide served as the etch stop. Finally, micrometer scale pores were patterned on the silicon membrane using photolithography followed by reactive-ion etching (RIE) on the nitride film and deep RIE (DRIE) to create micrometer scale pores on the silicon membrane. In more recent work that has received much attention, Tang and Lim et al. [10, 12] used two methods to fabricate holey silicon from an SOI wafer. The first method is nanosphere lithography using polystyrene spheres followed by DRIE etching of silicon using a chromium mask. The second method is based on block copolymer assembly to define features. Nanomesh films fabricated by Yu et al. [9], also from SOI wafers, used a well-known superlattice nanowire pattern transfer (SNAP) technique. Periodic structures fabricated at Sandia used a focused ion beam to create features [62]. The SOI wafer was first patterned and then plasma etched to release trenches in silicon. The buried oxide was removed using HF vapor. Finally, Marconnet et al. [8] used electron-beam lithography to fabricate a one-dimensional periodic holey structure.

Both steady-state and transient heating techniques have been used to measure temperature dependent thermal conductivity. Song et al. [7] used the steady-state Volklein technique [63] to measure in-plane thermal conductivity of thin films. Here a metal heater and thermometer are placed at each end of the suspended silicon thin film. They calculated the film thermal conductivity by measuring the temperature difference and estimating the heat flux along the film. Accurate estimation of heat flux requires knowledge of thermal conductivities of other materials in the device. More recent in-plane measurements [9, 10, 12] employed suspended heating and sensing platforms exploiting a technique developed by Li Shi [64]. Marconnet et al. [8] used a metal line as both heater and thermometer to measure the thermal conductivity of suspended silicon membrane beneath it. The device was constructed such that a simple 1D conduction model is valid. One obvious advantage is the precise determination of heat flux. For cross plane thermal conductivity determination, Hopkins et al. [61] used the time-domain thermoreflectance technique, in which a pump laser introduces a temperature perturbation and a probe laser detects the change in thermoreflectance.

The data cover porosities up to 40% with the limiting feature size spread over a broad range from 15 nm to 10 µm. Measured in-plane thermal conductivities at room temperature range from ~100 W/mK at 10 µm feature
size to \(\sim 2 \text{ W/mK} \) at \(15 \text{ nm} \) limiting features. Cross-plane thermal conductivities are \(\sim 10 \text{ W/mK} \) for \(\sim 500 \text{ nm} \) limiting feature size. The temperature trend shows distinct Umklapp peaks when limiting features \(>1 \mu\text{m} \). These peaks are noticeably absent in the data for smaller limiting features \((<100 \text{ nm}) \).

Figure 2.3 plots data for thermal conductivity of 2-D periodically holey silicon at room temperature. It is illustrative to first compare against predictions from continuum heat diffusion discussed in Section 2.1.1. Figure 2.3a plots the data as a function of the porosity and compares it against the Maxwell-Garnett model with cylindrical voids. The Maxwell-Garnet formula predictions exceed the measured thermal conductivities in all cases. Since this holds across different samples, feature sizes and measurement techniques, it is reasonable to assume that the explanation does not lie in measurement error. Rather the comparison suggests that sub-continuum phonon transport is indeed a factor in all samples.

As discussed in Section 2.1.3, the main difference between bulk and periodically holey silicon in terms of incoherent phonon transport, is in the relative importance of surface scattering. In the Casimir limit, the mean free path associated with surface scattering is the limiting dimension of the crystal. Figure 2.3b plots the intrinsic material thermal conductivity against the limiting dimension. A prediction of thermal conductivity assuming boundary scattering at the Casimir limit of completely diffuse scattering is also plotted. We obtain the Casimir limit by following Mingo’s modified Callaway model [16]. For large dimensions \((> 200 \text{ nm}) \) the data are close to the Casimir limit. However, for limiting dimensions below \(200 \text{ nm} \), the data fall significantly below the Casimir limit. It is worthwhile to note that a similar trend exists for nanostructured silicon in general and is not just special to periodic nanostructures. For example, a similar plot of thermal conductivity versus limiting size for silicon thin films and/or nanowires would reveal the same trend. As feature sizes shrink below \(100 \text{ nm} \), there is greater discrepancy between Casimir-limited and the measured thermal conductivities. However, it is not clear at present whether this trend has origins in the measurements themselves. Fabrication of features at the smaller end is clearly challenging and the presence of subtle defects such as at the boundaries is difficult to detect as well as rule out. Characterizations of the sample other than thermal
(a) The room temperature effective thermal conductivity of various 2-D periodic holey silicon nanostructures as a function of porosity. Open and closed symbols correspond to theory and experimental data respectively. The MG model is shown for comparison.

(b) Summary of room temperature intrinsic material thermal conductivity data of 2-D periodic structures plotted against the limiting dimension for surface scattering. The Casimir limit is shown for comparison.

Figure 2.3: Existing literature data as a function of porosity and limiting dimension. Measurement values reported as intrinsic conductivity are converted to effective conductivity using effective medium models and vice versa.
conductivity measurements, such as Raman scattering and high-resolution transmission electron microscopy, are not widely reported.

In the absence of detailed characterization beyond thermal measurements, various mechanisms have been suggested to explain the anomalously low thermal conductivities. These can be categorized into two: coherent and incoherent transport. A key hypothesis in coherent transport is that the periodic structure induces Bragg diffraction of phonons, opening up band gaps [9, 61]. While this may be expected at low temperature where the coherence length associated with long wavelength phonons can be large, this is inconsistent with the expected thermal coherence length of $L_c \sim 1 \text{ nm}$ at room temperature. We note that very recent calculations of the frequency dependent coherence lengths yield figures an order of magnitude larger. Partially coherent transport is another possibility where a part of the phonon population with coherence lengths comparable to or larger than the feature size exhibits coherent transport and phonons with shorter coherence lengths undergo incoherent diffusive transport. The arguments supporting incoherent transport rely on surface scattering with or without disorder as the mechanism responsible for reduced thermal transport. We first discuss the possibility of coherent transport in detail and then discuss incoherent transport theories from the literature.

Since phonon transport at room temperature is broadband, only modes whose coherence length is comparable to the feature size may possibly exhibit coherent effects. A simplistic estimate of the coherence length for thermal phonons is $L_c \sim v_s h/k_B T$. We note however, that the coherence lengths of individual modes with long wavelengths could be much larger than this figure. The key question is whether such modes have an appreciable impact on thermal transport. Recent work points both ways, further confusing the issue. Marconnet et al. [8] have argued that even in the extreme case that the coherent part of the spectrum corresponding to wavelengths comparable to the spacing does not contribute to thermal conductivity (i.e. coherent modes have zero transmission), the reduction in thermal conductivity at room temperature is negligible. They suggest that coherent transport may play a role only at much lower temperatures and would require periods and features on the order of tens of nanometers. On the other hand, Dechaumphai and Chen [20] have reported simulations of partially coherent transport to
show good agreement with the data of Yu et al. even for the very low thermal conductivities (\(\sim 2 \, \text{W/mK}\)). A key difference between the two is the criterion to decide coherent character. In the first case, coherence is assumed for modes with wavelengths comparable to or longer than the feature size. In the second case, coherence is assumed for modes whose Umklapp scattering limited mean free paths are larger than the feature size. The separation of modes into coherent and incoherent is arbitrary in both cases but critically affects the answer.

On the incoherent side, one explanation is the “necking” effect [65] where phonons with mean free paths larger than the size of the “necks” connecting the pores cannot transport heat as effectively as in the bulk. This is, in principle similar to the physical picture of particle diffusion in a lattice with residence time, discussed in Section 2.1.2. However, sub-continuum phonon transport rather than diffusive random walk is considered. The predictions from the model are larger than the measured conductivities. However, effects such as disordered pores, variance in pore size, surface disorder and roughness have not been considered and may serve to further reduce thermal conductivity to the observed values. Recent Monte Carlo simulations of the phonon Boltzmann transport equation using a mean free path sampling technique [19] yield an excellent match with the measured conductivities for limiting dimensions > 100 nm. Results from the simulations are included in Figure 2.3a. This provides strong support to the “necking” effect in incoherent transport as an important factor behind the reduced thermal conductivities.

While the effect of coherence at room temperature may be difficult to resolve without additional data and characterization, the temperature trend of existing data may provide clues on whether coherence is indeed a factor at low temperatures. The frequency dependence in the mean free paths should be different between coherent and incoherent transport leading to different temperature dependencies at low temperatures. Figure 2.4 plots representative thermal conductivity data versus temperature. For large features such as in the work of Song and Chen [7], a modified effective medium model that combines an analytical solution to the Boltzmann transport equation under the gray medium approximation [51], yields an excellent match with data over the entire temperature range. The MFP used depends on the choice of dispersion and is somewhat of a fitting parameter in these calculations. At
Figure 2.4: Thermal conductivity measurements of 2-D periodic structures versus temperature. Corresponding fitting curves are also shown. We note that the data from Yu et al. is rescaled to account for a disordered layer assumed in the Monte Carlo simulation.

On the other end of feature size, Ravichandran and Minnich [19] have reported Monte Carlo simulations of the Boltzmann equation over the entire temperature range using an efficient variance reduction technique. They assumed the presence of a disordered surface, which effectively increases the pore size. Using the thickness of the disordered surface, they are able to fit the thermal conductivity against the data of Yu et al. That surface disorder may play a significant role in reducing thermal transport in periodic structures has been previously suggested in the work of Lee et al. [21] though conclusive proof is missing. In their atomistic simulations of nanoscale pores on the order of a few nanometers spaced apart again by a few nanometers, it is found that the thermal conductivity is a strong function of the pore spacing. Further, not only porosity but also the ratio of the surface area of the pore to the volume of the crystal strongly affects thermal conductivity. However, in an overall sense, the emphasis on the magnitude of thermal conductivity rather than the slope of conductivity with temperature renders it difficult to provide a definitive answer on the issue of coherence.

One aspect that has not been studied in depth is the effect of disorder
In the period of the structure. In atomistic simulations [43] that are limited in system size to a few nanometers and therefore cut off larger phonon wavelengths, thermal conductivity does not appear to be sensitive to such disorder. This is expected in incoherent scattering. In coherent transport, however, we may expect a significant impact of disorder. To understand this, we can use the Helmholtz wave equation in the acoustic limit and consider multiple scattering of waves to show the impact of disorder. We solve the Helmholtz wave equation in the domain defined by silicon. Assuming the continuity of the displacement and stress at the silicon-hole interfaces, we formulate the scattered field as

$$\Psi_{\text{scat}}(r) = \sum_{i=1}^{N} \sum_{m=-\infty}^{\infty} A_{im} H_m(k|r - r_i|) e^{im\phi_{r,r_i}}$$  \hspace{1cm} (2.8)$$

where $A_{im}$ is the scattering strength of $m$th harmonic from the $i$th cylinder (centered at $r_i$) at a point $r = \{x, y\}$, $H$ is the Hankel function of the first kind, $\phi$ is a polar co-ordinate and $N$ is the number of cylinders. The coefficient $A_{im}$ is calculated by considering the acoustic impedance at hole-silicon interface and the multiply scattered wavefronts from all the other cylinders $j \neq i$. Specifically, in order to obtain $A_{im}$, we solve a hierarchy of equations:

$$A_{im} = iC_m F_{im},$$

where

$$F_{jn} = (-1)^n e^{ikr_j \cos \theta_j} + \sum_{i=1,j\neq i}^{N} \sum_{m=-\infty}^{\infty} iC_{m+n} F_{m+n} H_m(kr_{ij}) e^{im\phi_{ij}}$$  \hspace{1cm} (2.9)$$

The coefficient $C_m$ is obtained from the boundary condition at the hole-silicon interface and involves Bessel and Hankel functions. The treatment enables consideration of randomly arranged holes. The total field is the sum of incident and scattered field: $\Psi_{\text{tot}} = \Psi_{\text{inc}} + \Psi_{\text{scat}}$.

A simulation for scattering of a unit amplitude plane wave is done for an array of 25 holes of diameter 80 nm and pitch 150 nm for periodic and disordered configurations. The intensities of the scattered field at 0.3 and 3.0 THz with respective wavelengths of $\sim$ 18 nm and 1.8 nm are shown in Figure 2.5. The phonon field is incident from the top. When the array of holes is ordered, the field is either backward or forward scattered. At 0.3 THz the Rayleigh parameter has the same order of magnitude with unity,
corresponding to Mie scattering. Interference effects are evident. At 3 THz, Rayleigh parameter is much larger than 1 and geometric scattering occurs. Here, geometric shadowing effects are evident. As the array becomes more random, the field is scattered in other directions. Localized fields are evident at 0.3 THz where phase effects are appreciable since the period is comparable to the wavelength. The scattered field is “trapped” through multiple scattering events resulting in reduced transport along the direction of propagation. In localization theory, this attenuation of the field in the forward direction can be related to an effective mean free path though a formal theory for phonons is still in development. However, for the higher frequency, phase effects are less evident with increasing disorder since scattering is approximately in the geometric limit. We note that the experimental conditions for smaller features (<100 nm) correspond to the disordered case rather than the highly ordered case. It is not clear whether these effects are indeed present in the structures measured till date but such effects should be increasingly observable as feature sizes are further reduced.
2.2.2 Three-Dimensional Structures

Three-dimensional periodic dielectric structures have distinctive optical properties [66–68] and are of great interest in designing new functionalities in optoelectronics. They may also possess promising thermoelectric properties. In comparison to the top-down fabrication of 2D periodic structures, the fabrication of an ordered 3D structure is not as straightforward. Usually the fabrication uses a bottom-up approach that incorporates a self-assembled 3D structure. The opal structure is one example but has rather limited material options. It has also been shown that the negative replica of an opal give rise to better photonic band gap properties. Using opal as a template, one can deposit a variety of materials into the interstices to form the inverse structure. This enables applications beyond optics. For instance, carbon inverse opal, as a battery electrode, shows superior transport properties and mechanical integrity [69]. There are fewer attempts in thermal conductivity measurement than their 2D counterpart. We have measured polysilicon inverse opals with shell thickness down to 18 nm. The measurement details will be discussed in next chapter.

2.2.3 Transport in Non-Periodic Meso- and Nano-porous Structures

Porous silicon is one of the most studied meso-porous nanoporous structure. It is usually fabricated by electrochemical etching in aqueous or ethanoic HF solution [70, 71]. The morphology of porous silicon is generally classified by its pore size as nanoporous (< 2 nm), meso-porous (2-50 nm) and macro-porous (> 50 nm) [72]. In this section, we present an overview of thermal conductivity in porous silicon. The data are important in that they represent the limiting case for periodically holey structures that are essentially porous structures with ordered pores.

The first reported value of thermal conductivity for porous silicon at room temperature is 1.2 W/mK [73] for nano-porous silicon (40% porosity). In the same work, the thermal conductivity of as-prepared meso-porous silicon (45% porosity) was measured to be 80 W/m K which dropped to 2.7 W/m K upon
oxidation at 300°C. Temperature dependent measurements in the range of 35 K - 320 K using the 3ω method were first reported by Gesele et al. [74] The thermal conductivities of all the investigated samples increased with increasing temperature, and were less than 1 W/m K at room temperature. A minimum value of 0.03 W/m K was reported for p-type porous silicon with 89% porosity and 4.5±0.6 nm crystallite size. The ultra-low thermal conductivity in nano/meso-porous silicon is mainly attributed to strong phonon confinement and scattering at the crystallite boundary. Further, porosity also plays an important role in reducing the effective thermal conductivity, which can be explained by various effective medium theories mentioned in previous section. Theoretical approaches to model phonon transport in porous silicon include, for example, solution of the BTE by the discrete ordinate method [52], 3D Monte-Carlo simulations [75], molecular dynamic simulation [21, 43] and a combination of analytical and phonon-tracking methods [76]. It remains a challenge to clearly understand thermal transport in a non-periodic porous structure.

2.3 Conclusion

In conclusion, the reported room temperature thermal conductivities in periodically holey silicon are well below the Casimir limit corresponding to the limiting dimension. Current understanding of the physics responsible for such reduction points toward incoherent scattering of phonons at the surfaces of the pores and in the neck region connecting the pores for features >100 nm. Coherent effects may also play a role at lower temperatures and in smaller features. However, this is not clear at present and more work is necessary to first clearly define coherence for thermal phonons and then construct a theory for partially coherent phonon transport. From the perspective of applications, the thermal conductivities are attractive only at the very low end of the reported values. Thus, it is critical that these low values are carefully verified. Retaining the power factor close to the bulk in these structures remains challenging and has not been confirmed beyond the first report. A second interesting category of holey silicon material is the three-dimensional periodic structure. Inverse opals in particular are attractive for
future optics and battery applications. Thermal transport in these structures is well explained by the conventional incoherent diffusion of phonons. At low temperatures, however, phonons appear to scatter coherently with the thin grain boundaries in these structures. These materials can be promising for thermal applications provided their thermal insulating properties can be combined with improved mechanical properties at high porosity to create for example, lightweight and rigid thermal insulators.
In this Chapter, we first present a characterization scheme that integrates both electrical and thermal measurement. This method exploits the conducting nature of holey silicon for thermoelectric application, by supplying a current through the sample and measure the temperature change due to self-heating (Joule Effect). This self-heating method is validated by measuring a gold wire with high purity. Then we discuss the details in device fabrication and measurements. Finally, the focus of this chapter will be on the results followed by discussions.

3.1 Measurement Principle

In this section, we discuss our measurement principles and why they are essential to the overall device integration. Using this novel measurement technique, the fabrication complexity is greatly reduced, compared to an otherwise needed traditional thermal conductivity measurement platform.

3.1.1 Thermal conductivity $k$

We employ a frequency domain technique to measure the in-plane thermal conductivity of silicon thin films and holey silicon. It shares the same name (3ω method) but uses the sample itself as a heater and a temperature sensor [77]. The assumption that heat generated by Joule heating is equal to the heat flowing along the specimen requires the sample to be suspended in vacuum. A schematic of such configuration is shown in Figure 3.1. The sample is suspended and both ends are anchored on silicon dioxide. The
suspended portion has length $L$ and cross section area $S$. The gold electrodes are in contact with the sample to form a 4 point probe (4pp) configuration. The electrical contacts should be ohmic and have a resistance much smaller than sample resistance.

During the measurement, a sinusoidal current $I$ (at $1\omega$ frequency) is applied across the outer electrodes using the built-in sine output of a lock-in amplifier. A potentiometer with resistance much higher than sample resistance is connected in series to mimic a current source. This current sets up a $2\omega$ temperature oscillation due to Joule heating. For a sample with thermal diffusivity $\alpha = k/\rho C_p$ and time constant $\gamma = L^2/\pi^2\alpha$, the temperature distribution along $x$ is [77]:

$$T(x,t) = T_0 + \Delta_0 \sum_{n=1}^{\infty} \frac{[1 - (-1)^n]}{2n^3} \times \sin \frac{n\pi x}{L} \left[ 1 - \frac{\sin 2\omega t + \phi_n}{\sqrt{1 + \cot^2 \phi_n}} \right], \quad (3.1)$$

where $\cot \phi_n = 2\omega \gamma/n^2$, and $\Delta_0 = 2I_0^2 R/(\pi^3 k S/L)^1$ is the maximum dc temperature accumulation at the center of the sample. Note $\Delta_0$ is only $k$ dependent. Essentially, on top of the DC component, temperature fluctuates

\footnote{In the original paper, there is a typo in the denominator: '3' in $\pi^3$ was dropped incorrectly.}
at $2\omega$ as illustrated in Figure 3.2. The amplitude of this fluctuate, $\Delta T_{2\omega}(x)$, is maximum at the center, and 0 at both ends. Macroscopically, this fluctuation is averaged along $x$ and reflected in resistance shown below.

Because the sample resistance is linearly dependent on temperature in the range of interest, there will be a resistance fluctuation:

$$
\delta R = \frac{dR}{dT} L \int_0^L [T(x,t) - T_0] dx \\
= \frac{dR}{dT} \Delta_0 \sum_{n=1}^{\infty} \frac{[1 - (-1)^n]^2}{2\pi n^4} \left[ 1 - \frac{\sin 2\omega t + \phi_n}{\sqrt{1 + \cot^2 \phi_n}} \right].
$$

(3.3)

Combined with the original $1\omega$ current, the voltage across sample will have a $3\omega$ component. Note inside the summation, the terms decrease with $n^4$ and numerator is 0 when $n = 2$. Therefore it only introduces a relative error of $\sim 3^{-4}$ if we only keep the $n = 1$ term and drop the rest. Now the time domain $3\omega$ voltage becomes:

$$
V_{3\omega}(t) \approx -\frac{dR}{dT} \frac{2I_0^3 LR}{\pi^4 kS \sqrt{1 + (2\omega \gamma)^2}} \sin(3\omega t - \phi),
$$

(3.4)

where

$$
\tan \phi \approx 2\omega \gamma.
$$

(3.5)

Here, $\phi$ is the phase of $3\omega$ signal, i.e. $\tan \phi$ is the ratio between the out-of-phase and in-phase signal. Since the $3\omega$ voltage is picked up by a lock-in
amplifier with high dynamic reserve, they display as the root-mean-square (RMS) values of the oscillation. To accommodate this convention, we can rewrite Eq. 3.4 as:

$$V_{3\omega,\text{rms}} \approx \frac{dR}{dT} \frac{4I_{3,\text{rms}}^3 LR}{\pi^4 k S \sqrt{1 + (2\omega \gamma)^2}}. \quad (3.6)$$

In the rest of the chapter, unless otherwise noted, $V$ and $I$ are all RMS values.

For a fixed frequency $\omega$ or in the limit of $2\omega \gamma \to 0$, the $3\omega$ voltage $V_{3\omega}$ is proportional to the cubic of $1\omega$ current $I_0^3$. This linear dependency is an important validation of the measurement and can be used to find the thermal conductivity $k$. In the moderate frequency regime, i.e. $2\omega \gamma$ is comparable to 1, $V_{3\omega} \propto 1/\sqrt{1 + (2\omega \gamma)^2}$, and we can use Eq. 3.5 to get the thermal diffusivity.

To demonstrate this technique in our lab, we measured the thermal conductivity of a suspended gold wire. The electrical resistance is calibrated against temperature to get the temperature coefficient $dR/dT$. We use a lock-in amplifier (SR830) to detect the voltage at $3\omega$. Since SR830 has a high dynamic reserve (>100dB) and is able to pick up the $3\omega$ voltage from the large background $1\omega$ signal, we did not use any noise cancellation scheme, such as nulling a bridge. Figure 3.3a shows $3\omega$ voltage signal versus the cubic of $1\omega$ current (3 Hz) at 300K, which clearly shows the characteristic linear relationship. The slope of the curve is used in Eq. 3.6 to obtain thermal conductivity $k$. At $\omega = 3$ Hz, $\tan \phi \approx 2\omega \gamma \to 0$. Therefore given the resistance and geometry, we can determine $k$. It is found to be $327 \pm 16$ W/mK at 300 K, compared with industry standard of 317 W/mK. Further, we calculated the Lorenz number to be $2.51 \times 10^{-8}$ WΩK$^{-2}$, very close to the reported value of $2.44 \times 10^{-8}$ WΩK$^{-2}$. The temperature dependent thermal conductivity is shown in Figure 3.3b, with similar trend as industry standard.

Figure 3.3c shows the frequency dependence of $V_{3\omega}$ (left axis) and $\tan \phi$ (right axis). The fitting curves are from Eq. 3.5 and 3.6. From the fitting process, we obtained the gold wire thermal diffusivity to be $1.277 \text{ cm}^2/\text{s}$, which is in consistency with the reported value of $1.270 \text{ cm}^2/\text{s}$.

35
(a) $3\omega$ voltage signal is proportional to the cubic of $1\omega$ current (3 Hz) at 300K

(b) Comparison between measured thermal conductivity and industry standard

(c) $3\omega$ voltage and $\tan \phi$ are plotted against frequency at 300 K. The thermal diffusivity can be extracted from this plot.

Figure 3.3: $3\omega$ measurement validation using a suspended gold wire.
3.1.2 Seebeck coefficient $S$

One major advantage of this method is that the fabrication process is substantially less complicated compared with a recent study which accomplishes the same thermoelectric measurement [12], and we can easily incorporate a platform for Seebeck coefficient measurement.

Seebeck coefficient of a material is defined as:

$$S = -\frac{\Delta V}{\Delta T},$$

(3.7)

where $\Delta V$ is open circuit thermoelectric voltage and $\Delta T$ is the temperature difference between two terminals. The negative sign is a convention such that p-type materials have positive $S$ and n-type materials have negative $S$. From a measurement perspective, we need to do the followings:

1. Create a temperature gradient across the sample
2. Measure the temperature difference between two terminals
3. Measure the voltage drop between the two terminals where $\Delta T$ measurement is performed.

We follow a similar approach described in literature [78] but with major modifications to improve accuracy and speed up the whole process. In addition to use a frequency domain heating technique, we also employed frequency sensing on both temperature sensors, as opposed to DC sensing in Ref. [78]. Time consumed in measurement is substantially reduce because the system reaches steady state faster and DC technique. The accuracy is also improved as we will discuss in following sections. The measurement scheme is depicted in Figure 3.4.

A metallic heater is placed at one end of the sample and supplied with a sinusoidal heating voltage $V_h$ and current $I_{h,1\omega}$. A temperature field with frequency $2\omega$, $T_{2\omega}$ is built up in the direction indicated above. This temperature profile is hard to theoretically predict due to the complexity of material geometry. However, we can measure it at the two ends of sample, where we place two RTD sensors: 1 and 2 as shown in the figure. In DC sensing scheme [78], the sensor resistance is measured at several $V_h$ values and subtract resistance at $V_h = 0$ to get $\Delta R$ hence $\Delta T$. This could potentially in-
Figure 3.4: Schematic for measurement of Seebeck coefficient in frequency domain. All the lock-in amplifiers have the same reference input. $V_{2\omega}$ (across sample) and $V_{3\omega}$ (across sensor) are taken for each heating voltage $V_h$.

Introduce big uncertainties as $\Delta R$ is derived from the subtraction between two very similar values. Depending on the precision of instruments, we found the uncertainty of this method is between 50% and 100%. Another concern is the hysteresis of sensor resistance. It contributes significantly to uncertainty in our case as temperature rise is typically less than 1 K. Moreover, it also takes longer for the system to reach steady state for each heating voltage.

In frequency domain, $\Delta R$ and $\Delta T$ are directly probed using the third harmonic. We send a sensing current through sensors at the same $1\omega$ frequency and in sync with heating voltage $V_h$. Note the frequency $\omega$ should be small such that the phase difference between two sensors is negligible. In our case, $\omega < 100$ Hz. Due to the established $2\omega$ temperature field, a voltage with $3\omega$ component across the sensor is established and picked up by lock-in amplifier. From this third harmonic voltage, we can find the $\Delta T$ at this location using the following equation:

$$\Delta T = 2 \frac{dT}{dR} \frac{1}{I_s} V_{3\omega}. \quad (3.8)$$
Because RHS of Eq. 3.8 has the ratio between two RMS values $V_{3\omega}/I_s$, the obtained $\Delta T$ is the amplitude of the oscillation. We can then sweep heating voltage to get the relationship between $\Delta T$ and $V_h$,

$$\Delta T = \alpha V_h^2.$$ (3.9)

For the difference in temperature rise between two sensors, $\Delta T_{1,2} = \alpha_{1,2} V_h^2$. We will use $\Delta T$ and $\alpha$ for simplicity in the rest of this chapter.

Now we discuss the measurement of thermoelectric voltage $\Delta V$. The RTD sensors are also in electrical contact with the sample. With the $T_{2\omega}$ temperature field, there will exist $\Delta V$ oscillating at $2\omega$ due to Seebeck effect. We use a lock-in amplifier to measure this $V_{2\omega}$ with a reference signal feed from the heating voltage $V_h$. There is a $90^\circ$ phase difference in $2\omega$ signal with the reference sine-out voltage from lock-in amplifier. Again, we do a heating voltage sweep and obtain the corresponding Seebeck voltages. Now the relationship between $V_{2\omega}$ and $V_h$ is

$$V_{2\omega} = \beta V_h^2.$$ (3.10)

From Eq. 3.9 and 3.10 and can obtain the magnitude of Seebeck coefficient $S$:

$$|S| = \frac{\sqrt{2}\beta}{\alpha},$$ (3.11)

where the constant $\sqrt{2}$ comes from the fact that $\Delta T$ in Eq. 3.9 is amplitude and $V_{2\omega}$ in Eq. 3.10 is RMS value. The sign of $S$ (dopant type in silicon) can be obtained by doing the same measurement in DC mode.

### 3.2 Integrated Measurement Device Fabrication

To measure all three thermoelectric properties on one sample, we need to combine the two techniques mentioned above. The new platform can be seen as an extension from Figure 3.1. A serpentine metallic heater is added near one side of the sample on silicon dioxide. By adding 4 contact pads to each, two inner electrodes are converted into RTD sensors to measure temperature. Just by these simple modifications, the new device is capable of measuring
Thinner barrier layer yields more silicon consumption during doping process. The original device layer thickness is \( \sim 205 \) nm for all samples. Thickness measurement was carried out using ellipsometry.

The fabrication flow is shown as schematic in Figure 3.6. We start with an silicon-on-insulator (SOI) wafer with \( \sim 200 \) nm device layer and 400 nm of buried oxide (BOX). The device layer is doped with phosphorous in a diffusion doping furnace using a two-step method: pre-deposition (pre-dep) at 950 °C for 10 min followed by drive-in at 1100 °C for 6 min). Prior to doping, a thin layer of silicon dioxide (5, 10, 15, 20 nm) is deposited on 4 wafer chips. The purpose of this silicon dioxide layer is to protect the surface, and provide a barrier layer for diffusion doping. The deposition is done using PECVD and characterized by ellipsometry. At 950 °C, the bulk solubility of phosphorous atoms in silicon is \( 7.8 \times 10^{20} \) cm\(^{-3} \) [79], more than one order of magnitude higher than optimal concentration for silicon thermoelectrics. Those barrier layers slows down the diffusion process and also provides a search grid for optimization. After the pre-dep step, phosphosilicate glass is removed in diluted HF. The sample is then placed in 1:1 HNO\(_3\):H\(_2\)SO\(_4\) solution to oxidize remaining phosphorous atoms at the surface for 10 mins, followed by dipping in diluted HF again. The remaining device layer thickness
After device release, chip is mounted to a ceramic chip holder and wire-bonding is performed to make electrical connection to measurement instruments.

is characterized using ellipsometry, and is plotted against the original barrier layer thickness in Figure 3.5.

During the doping process, the reaction $2P_2O_5 + 5Si \rightarrow 5SiO_2 + 4P$ consumes Si into SiO$_2$ which is then removed by HF. A thicker barrier layer hinders the diffusion of $P_2O_5$ to reach device layer. As a result, chip with thinner barrier layer has a thinner device layer after the process as shown in Figure 3.5.

A thin layer of SiO$_2$ ($\sim 75$ nm) were deposited for insulation purposes. Larger features (e.g. contact pads and alignment markers) were defined by photolithography whereas smaller ones (electrodes, heaters and RTD sensors) were patterned using E-beam lithography. Between the two metallization steps, 3% HF removes insulation oxide such that device layer is in contact with electrodes. We evaporate 5 nm of chromium as adhesion layer and 300 nm gold. To achieve ohmic contact, the device is annealed at 300 °C for 5 min in N$_2$. It is found that all samples except the one with 20 nm barrier layer already achieved ohmic contacts with small contact resistance before annealing. After annealing, the improvement in contacts is not significant. For the sample with 20 nm barrier layer, ohmic contacts are achieved after
annealing but contact resistance is not extracted due to large overall resistance.

![Figure 3.7: Top SEM for samples with 3 different porosities: 12%, 38% and 51%. The scale bar is 1 µm and same for all three samples.](image)

Next, we use e-beam lithography and DRIE to pattern holes followed by device suspension using diluted HF (3%) to undercut BOX layer. Resist used in e-beam lithography is PMMA (polymethyl methacrylate) with 950k molecular weight (MW) in Anisole. The solid ratio is 2% (i.e. PMMA 950k A2). After spinning at 2500 rpm and post-baking at 180 °C for 2 min, the resulting thickness is ∼150 nm. I used dot patterns and varying dosage to create holes of different sizes onto PMMA. The DRIE process is calibrated to have a sufficient selectivity between silicon and PMMA. During DRIE process, we employed an alternating process with etching and passivation steps to protect the side walls. The top view SEM of 3 typical holey samples with different porosity are shown in Figure 3.7.

![Figure 3.8: The procedure to determine porosity. Average diameter and necking distance can also be determined from the particle size/area. Note particles are not a perfect circles, and the actual limiting dimension is smaller than what is determined by this method.](image)

We determine the porosity of each sample from those SEM images and the
procedures are shown in Figure 3.8. The SEM is first loaded into ImageJ and converted to a binary image. The area of each circle is recorded and average diameter is determined. The porosity is simply the ratio between black area and the whole area of the image. Figure 3.9 shows the diameter distribution of samples with porosity 12% and 38%. The mean diameters are 120 nm and 230 nm respectively.

For the final releasing step, we found that buffered oxide etch (BOE) etches heavily-doped silicon and produces porous-like structure with nano-pores, which degrades electrical properties after etching BOX. Therefore it is not suitable for the final device release. This may be due to the weak oxidation agent of NH$_4^+$ ions in BOE. Therefore, we use diluted HF instead. We also found that even in diluted HF (3%), while the electric property of sample does not degrade, the electrical contact resistance between metal electrodes and doped silicon becomes significantly larger. Therefore, we used a PMMA mask to cover the contacts during device releasing in HF (3%). The final device is therefore transferred to acetone and then IPA, and subsequently went through a CO$_2$ super critical drying process to minimize surface tension. Finally, we use oxygen plasma to remove any remaining PMMA residues. The suspended structures are shown in Figure 3.10.
Figure 3.10: Tilted view SEM shows successful suspension of holey silicon with 2 porosities: 12% and 38%. Not all area in the zoomed-in image is under focus due to stage tilt and shallow field of depth.
The bottleneck of the whole process is the final releasing step. Even with supercritical drying, the surface tension is still present due to system imperfection. In Figure 3.11, two common failure modes are shown. The suspended structure could either collapse onto the substrate or be completely destroyed by surface tension.

Figure 3.11: Device failure during final releasing step. Left: Periodic porous structure collapsed onto silicon substrate. Right: Porous structure was almost completely destroyed by surface tension.

3.3 Measurement Results

In this section, we will present our raw measurement data and deliver detailed analysis towards final results of the three thermoelectric properties. We start with electrical conductivity and Seebeck coefficient.

3.3.1 Electrical conductivity $\sigma$

We confirmed ohmic contacts for devices made with all 4 barrier layer thicknesses. However, for the one with 20 nm barrier thickness, the resistivity is $\sim 1\ \Omega\cdot\text{cm}$, much larger than the other three, which are between 1-10 m$\Omega\cdot\text{cm}$. A summary of electrical conductivity measurement is presented in 3.1. All the measurements were taken on solid thin film samples, therefore they are representative to the corresponding device.
Table 3.1: Summary of electrical conductivity measurement at 300 K. For each barrier layer thickness, resistivity values are taken from solid thin films. There are two chips with 15 nm barrier layer (post deposition measurement shows 16 nm for one chip).

<table>
<thead>
<tr>
<th>Barrier layer thickness, nm</th>
<th>Resistivity $\text{m}\Omega\cdot\text{cm}$</th>
<th>Estimated doping $\text{cm}^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.09</td>
<td>$8.0\times10^{19}$</td>
</tr>
<tr>
<td>10</td>
<td>1.98</td>
<td>$3.6\times10^{19}$</td>
</tr>
<tr>
<td>15</td>
<td>4.53</td>
<td>$1.3\times10^{19}$</td>
</tr>
<tr>
<td>16</td>
<td>6.57</td>
<td>$8.0\times10^{18}$</td>
</tr>
<tr>
<td>20</td>
<td>$\sim$ 1000</td>
<td>$1\times10^{16}$</td>
</tr>
</tbody>
</table>

The effective resistance of a typical holey silicon sample is shown in Figure 3.13. This particular sample was made with 15 nm barrier layer and has hole of diameter $\sim$ 230 nm. The critical dimension is $\sim$ 120 nm and porosity $\sim$ 38%. After factoring in the geometry, the effective resistivity is $\sim$ 10.04 m$\Omega$·cm at 300 K, as shown on the right axis in Figure 3.13. Using effective medium theory Eq. 2.6, we obtained intrinsic material resistivity to be 4.35 m$\Omega$·cm at 300 K, compared with 4.53 m$\Omega$·cm for the corresponding solid thin film sample. At this critical dimension ($\sim$ 120 nm), we don’t expect to see strong boundary scattering that impacts mobility. It has also been observed that mobility remain identical to bulk value in device layers with
Figure 3.13: Electrical resistance of a typical holey silicon membrane from 300 K to 440 K. The dashed line is linear fitting, whose slope is $dR/dT$. The right axis indicates the effective resistivity.

thickness down to 50 nm in SOI [80]. Assuming bulk mobility, the estimated carrier concentration is therefore $1.3 \times 10^{19}$ cm$^{-3}$. The estimation procedure of doping concentration is similar for other samples.

Above 300 K, heavily doped silicon shows metallic behavior as resistance increases linearly with temperature. This property enables us to use it as a RTD sensor later on in thermal measurement.

For all the holey samples we have measured electrical resistivity on, we compare it with resistivity of a non-holey sample from the same chip. Because samples from same chip underwent the exact same fabrication processes, we assume the same doping concentration for those samples. Therefore we can compare the resistivities and observe/assess the porosity effect. In Figure 3.14, the ratio between effective conductivity $\sigma_{eff}$ (derived from holey samples) and material conductivity $\sigma_0$ (derived from non-holey samples) is plotted against porosity. For comparison, a curve representing EMT with cylindrical voids (Eq. 2.6) is also included. We can see that for porosities less than 40%, the ratio follows the predicted curve. This small discrepancy is an indication that mobilities for holey and non-holey samples are indeed similar. At those porosities, the limiting dimension is $> 120$ nm. As discussed in Section 1.2.2, we don’t expect boundary scattering will have a big
Figure 3.14: Ratio between effective and material conductivity plotted as a function of porosity. The curve is from effective medium theory discussed in Section 2.1.1.

impact at this length scale.

3.3.2 Seebeck coefficient $S$

Figure 3.15 shows the $3\omega$ voltages across two sensors as a function of $V_h^2$ between 300 K and 420 K. The linear relationship reveals the quadratic dependence in Joule heating. The slope of linear fit is used in Eq. 3.8 to get $\alpha$ values in Eq. 3.9. It is also worth noting that as temperature increases, the slope also increases, suggesting a slight change in overall heat transfer equations. This is expected as substrate materials change their properties with temperature.

Figure 3.16 displays the $\alpha$ values derived from the slopes in Figure 3.15 and Eq. 3.8. The black, red and green symbols represent sensor 1, sensor 2 and their difference from 300 K to 420 K. All the values are below 0.15 K/V^2 and the difference is smaller than 0.5 K/V^2. Even for the largest heating power used in the experiment, the DC component of temperature rise is limited to 2 K, and temperature difference across sample is smaller than 1 K.
Figure 3.15: Raw $3\omega$ voltage across sensor 1 (top) and sensor 2 (bottom) as a function of $V_h^2$ from 300 K to 420 K. Using the slope of linear fitting curve and Eq. 3.8, we can get $\alpha$ in Eq. 3.9.

Figure 3.16: The $\alpha$ values for sensor 1, sensor 2 and their difference from 300 K to 420 K.
Figure 3.17: The amplitude of temperature oscillation at sensor 1 (black) and sensor 2 (red) as a function of heating voltage. The cryostat bath temperature is 300 K.

This requirement ensures the quantity measured is the property at the bath temperature of the cryostat with $< 2$ K uncertainty.

To further illustrate temperature oscillation at each heating voltage, let’s look at Figure 3.17.

The dashed lines are quadratic fittings for each sensor. Note at zero heating voltage, there is a finite temperature rise. This is due to the self-heating effect from sensing current. Theoretically, one can apply a small enough sensing current to avoid self-heating. However, given Eq. 3.8 the $3\omega$ voltage signal would be too small and prone to noises in that case. This self-heating effect is constant no matter what the heating voltage is, therefore it does not affect the final result.

Figure 3.18 shows the $2\omega$ voltages across a sample as a function of $V_h^2$ at 300 K and 420 K. Once again, we see a linear relationship with the heating power for each temperature. As temperature increase, the slope of each linear fitting also increase.

Figure 3.19 plots the $2\omega$ voltage against temperature difference $\Delta T$ across a sample, which is obtained from Figure 3.17. Since $\Delta T$ is amplitude and $V_{2\omega}$ is RMS value, we need to multiply a factor of $\sqrt{2}$ to the slope of the
Figure 3.18: Raw $2\omega$ thermoelectric voltage across sample as a function of $V_n^2$ from 300 K to 420 K. The slope of linear fitting curve is $\beta$ in Eq. 3.10.

Figure 3.19: $2\omega$ voltage against temperature difference $\Delta T$ across a sample at 300 K.
Table 3.2: Sample summary of Seebeck coefficient measurement

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Estimated doping cm$^{-3}$</th>
<th>Porosity</th>
<th>S @ 300 K $\mu$V/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid thin film</td>
<td>$8.0 \times 10^{18}$</td>
<td>0</td>
<td>-273</td>
</tr>
<tr>
<td>Periodic holey</td>
<td>$1.3 \times 10^{19}$</td>
<td>38%</td>
<td>-241</td>
</tr>
<tr>
<td>Periodic holey</td>
<td>$3.6 \times 10^{19}$</td>
<td>38%</td>
<td>-186</td>
</tr>
<tr>
<td>Solid thin film</td>
<td>$3.6 \times 10^{19}$</td>
<td>0</td>
<td>-178</td>
</tr>
<tr>
<td>Periodic holey</td>
<td>$8.0 \times 10^{19}$</td>
<td>38%</td>
<td>-135</td>
</tr>
</tbody>
</table>

linear fit in order to get the Seebeck coefficient. It is also worth pointing out that the extraction method described here is equivalent to Eq. 3.11 in Section 3.1.

The measured Seebeck coefficients for 5 samples with different doping concentrations are summarized in Table 3.2. One notable comparison is between solid thin film and periodic holey silicon samples on a same chip with same doping concentration at $3.6 \times 10^{19}$ cm$^{-3}$. Their Seebeck coefficients are found to be almost identical given uncertainty, which are 186 $\mu$V/K and 178 $\mu$V/K respectively at 300 K. Therefore we may conclude that Seebeck coefficient does not vary substantially with porosity for the given length scale.

The temperature dependent Seebeck coefficient is shown in Figure 3.20. The plotted values are for non-holey ($8.0 \times 10^{18}$ cm$^{-3}$), and holey silicon with 38% porosity ($1.3 \times 10^{19}$ cm$^{-3}$, $3.6 \times 10^{19}$ cm$^{-3}$, $8.0 \times 10^{19}$ cm$^{-3}$). The values are considerably lower than reported bulk values for similar doping concentration [81]. Never the less two general trends can be inferred from the figure. Across different samples, $S$ is higher for low doping concentrations. This observation is in agreement with other measurements on bulk and silicon nanostructures, as discussed in Section 1.2.3. For each sample, $S$ increases with temperature. This trend suggests that in those samples, the diffusion part dominates over phonon drag. Detailed discussion will be provided in later section.
3.3.3 Thermal conductivity $k$

As for thermal conductivity, I measured three different samples in total: One solid thin film sample and two holey silicon samples. The solid thin film sample has a width of 1 $\mu$m and thickness 190 nm. Two holey samples have an average neck distance of 230 nm and 120 nm, and porosity of 12% and 38% respectively. The pitch is 350 nm. Sample dimensions are summarized in Table 3.3 below. For the two holey samples, the estimated doping concentration is $\sim 1.3 \times 10^{19}$ cm$^{-3}$ while the solid sample is $2 \times 10^{20}$ cm$^{-3}$.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Thickness nm</th>
<th>pitch nm</th>
<th>Hole $\varnothing$ nm</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid thin film</td>
<td>190</td>
<td>NA</td>
<td>NA</td>
<td>0</td>
</tr>
<tr>
<td>Periodic holey</td>
<td>195</td>
<td>350</td>
<td>120</td>
<td>12%</td>
</tr>
<tr>
<td>Periodic holey</td>
<td>195</td>
<td>350</td>
<td>230</td>
<td>38%</td>
</tr>
</tbody>
</table>

Figure 3.21 plots the as measured $3\omega$ voltage against the cubic of $1\omega$ current for a typical sample between 300 K and 420 K. The characteristic linear relationship in Eq. 3.6 is clearly present. As we increase temperature, the
Figure 3.21: $3\omega$ voltage across a sample as a function of the cubic of $1\omega$ current between 300 K and 420 K.

signal shows same trend but with a larger slope. Figure 3.22 shows the data with error bars at one temperature, 300 K. The error bar is 3 times the standard deviation ($3\sigma$) from measurement.

The obtained thermal conductivity is plotted in Figure 3.23 from 300 K to 420 K for solid thin film and the aforementioned holey silicon samples. For comparison, we included data of heavily arsenic doped silicon substrate (measured by conventional $3\omega$ method) and intrinsic bulk data. The $k$ values for periodic holey silicon sample are material thermal conductivities converted using Eq. 2.6 with corresponding porosities.

The primary source of error arises from the uncertainty of temperature coefficient of sample resistance and the inverse slope of $V_{3\omega}$ against $I^3$. While the measurement of resistance or $3\omega$ voltage usually has less than 0.5% error, the uncertainty is amplified when taking the derivative (in our case, the derivative is the slope due to linear relationship.) We use $R$ to fit a linear model and find the 95% confidence interval of the slope, which is the estimated coefficient $\pm$ two standard errors. It is found that the confidence interval is always within the 10% uncertainty of the nominal value. Therefore, we use the upper bound 10% to estimate the measurement error in aforementioned two slopes.
Figure 3.22: Linear fit for $3\omega$ voltage w.r.t the cubic of $1\omega$ current at 300 K

Figure 3.23: Material thermal conductivity of thin film silicon and two holey silicon samples. Data for intrinsic bulk silicon and heavily doped bulk silicon are shown for comparison.
Another source of error comes from the assumption that the two sample ends are at the substrate temperature. Such assumption would be invalid due to the following reasons: high thermal contact resistance, high thermal resistance of box layer and additional Joule heating at the contacts due to electrical contact resistance. We estimate the thermal resistance of contacts and box layer to be less than 1% of sample thermal resistance if the sample $k$ is 40 W/mK. This 1% is the upper bound since the actual samples have smaller $k$. We also obtained electrical resistance from 4pp and 2pp measurement and always found it to be less than 10% of the sample electrical resistance. Now the temperature rise at contacts would be $\sim I^2(R_s + R_c)R_{dc}$ which is about 1.1% of the average temperature of the sample $\sim I^2(R_s)R_{ts}$.

Other sources of error include geometry measurement from SEM, thickness measurement from ellipsometry and porosity estimation from image analysis. We estimate the overall error to be within 5%. Therefore, the upper bound of the overall error in material thermal conductivity $k$ would be $\sqrt{10\%^2 + 10\%^2 + 1.1\%^2 + 5\%^2} \sim 15\%$. Here we assume all the errors are independent and their covariance is 0.

While bulk silicon has a thermal conductivity of 148 W/mK at 300 K, $k$ reduces to 91 W/mK when doped with As at $5 \times 10^{19}$ cm$^{-3}$ due to enhanced phonon scattering with impurities and electrons. $k$ for solid thin film is 37 W/mK, about a quarter of the bulk value. The thermal conductivity values for two holey samples are 26 W/mK and 12 W/mK respectively. The less porous one has a neck distance of 230 nm and a thickness of 195 nm, hence the limiting dimension shall be the thickness. With similar limiting dimension, the thermal conductivity is only 70% of the thin film sample. Clearly, those periodic holes have a significant impact to the overall phonon transport. The other porous sample (38% porosity, 120 nm limiting dimension) has the smallest measured thermal conductivity: 12 W/mK, which is about 8% and 32% of bulk and thin film values respectively.

As temperature increases, more phonons participate in the three-phonon process hence Umklapp scattering becomes stronger. As a result, thermal conductivity decreases with temperature as evident in both cases of bulk samples. However, this trend is less obvious in all 3 silicon nanostructure samples, suggesting a weaker contribution from Umklapp scattering. In fact,
the sample with bigger porosity, thermal conductivity remains relatively flat with respect to temperature in the given range. We also note that the thermal conductivity for both samples are 30-40% smaller than corresponding Casimir limit with critical dimensions of 195, 120 nm, as shown in Figure 3.24. This discrepancy could be caused by several reasons: stronger impurity (dopant) and electron scattering, coherent phonon scattering with periodic holes and etc. It will be discussed in details in following section.

3.4 Discussion

3.4.1 Thermal conductivity $k$

We now discuss thermal conductivity. Apart from the common scattering rates discussed in Section 2.1.3, there are additional phonon interactions in heavily doped silicon nanostructure. Previously, mass difference scattering only accounts for silicon isotopes. As the dopant usually has a bigger mass difference and its concentration can be as high as one in thousand, the effect
on phonon transport is much more significant than isotopes. This scattering process can be modeled as:

$$\tau_m^{-1} = V_0 \Gamma / (4 \pi v_s^3) \omega^4,$$

(3.12)

where $v_s$ is sound velocity, $V_0$ is the volume per atom, and $\Gamma$ is defined as $\Gamma = \sum_j f_j (1 - M_j/M)^2$. Here, $f_j$ is the percentage of atom type $j$, whose mass is $M_j$, and $M$ is the average atomic mass. In our case, $M_{Si}=28$ and $M_P=31$.

With the high doping required in thermoelectric applications, phonon-electron scattering, which is otherwise neglected, assumes importance. In modeling the thermal conductivity of doped silicon nanostructure, Asheghi et al. [82] employed a deformation potential to calculate the phonon-electron interaction. However, the deformation potential was fit at each doping level, which reduces the physical significance of the model. In a different paper, Zou [83] assumed the scattering rate to be linear with the carrier concentration, which is only valid at low but not high doping levels. Here we develop a new expression that accounts for low as well as high doping without fitting parameters. It is also worth pointing out that this expression is important in later sections for Seebeck effect.

We start with the transition rate used in the calculation of electron relaxation time due to phonon scattering [84]:

$$S(p, p') = \frac{\pi m D_A^2}{\hbar \rho v_s p V} \delta \left( \pm \cos \theta + \frac{\hbar q}{2p} \mp \frac{\omega}{v_e q} \right),$$

(3.13)

where $p, p'$ are the momentum of an electron before and after scattering, $\theta$ is the angle between the two directions, $D_A$ is the magnitude of the deformation potential, $\rho$ is the density of silicon, and $V$ is a normalization volume. The $\delta$-function ensures momentum and energy conservation. High frequency phonons are unlikely to be scattered as electrons in the conduction band of $n$-type silicon are only thermally excited and do not possess sufficient energy. Due to symmetry, only longitudinally polarized phonons scatter electrons [85]. Instead of summing over the phonon wave number as in the case of electron transport, we sum the transition rate over spins, valleys and all final electronic states to evaluate the phonon relaxation time due to electron
Figure 3.25: Thermal conductivity as a function of doping concentration at 300 K. The open circles, triangles and squares are measurement values from Ref. [82, 86, 87]. The red, green and blue curves are calculations for P-doped 3 $\mu$m thick, As-doped 174 nm thick, and As-doped 74 nm thick single-crystal silicon films respectively.
scattering,
\[ \tau_{p-e}^{-1} = \sum_{\uparrow, \text{valley}, p'} S(p', p') f(p)(1 - f(p')). \] (3.14)

Here, \( f(p) \) is the probability of an available electron to be scattered while \( (1 - f(p')) \) is the probability of availability of the final state to be scattered into. Noting that electrons have the same spin and remain in the same valley before and after the scattering process, summations over spins and valleys give degeneracies of 2 and 6 respectively. After the summation, \( \tau_{p-e} \) is only a function of the phonon wave number \( q \).

We set the deformation potential, \( D_A \) to 9 eV, which is the value determined from fits to mobility data [22]. Figure 3.25 compares the available experimental data for n-doped silicon films with calculations. The predictions agree well with the data which, however, are a limited set. We note that the agreement arises without any specific fitting to doping dependent thermal conductivity data.

We now turn to our measurement data. The clear lower-than-Casimir trend is across all three sample. For the thin film sample, adding dopant and
electron scattering fits the data and the temperature trend. However, same statement is not true for the other two periodic porous samples. Even after accounting for the additional scattering mechanism, the reduction in $k$ is not fully explained. As discussed in Chapter 2, it is not surprising to observe thermal conductivity below Casimir limit in silicon nanostructures [4–13]. Tang et al. reported 10.23 W/mK as room temperature $k$ with very similar structure to ours. Their pitch is 350 nm and average neck distance is 152 nm.

Even though we are referring limiting dimension for both nanowires (diameter) and holey silicon (neck distance), it is important to distinguish the different from those two. In holey silicon system with hexagonal pattern, phonons experience more backward scattering from hole sidewalls. This difference could be the reason for below-Casimir thermal conductivity. Therefore, we can define a characteristic length $l_c$ for phonon transport, which is smaller than the limiting dimension, and use $l_c$ as a fitting parameter in boundary scattering.

It is found $l_c = 120$ nm and 40 nm respectively for two holy samples with limiting dimension 230 nm and 120 nm, porosity 12% and 38%. From this limited dataset, the reduction of $l_c$ from limiting dimension is positively correlated with porosity. For a porosity of 38%, there is a 3-fold reduction from limiting dimension to $l_c$ while for a porosity of 12%, the reduction is only about 2-fold.

In light of our electrical conductivity measurements, it is unlikely to have enough defects that significantly scatters phonons in the samples. Therefore, we hypothesis the holes in our periodic porous silicon thin film are the main scatter for phonons. A recent measurement [14] suggests possible coherent scattering for phonons with MFP longer than a threshold value, and the authors were able to empirically construct a hybrid model to explain their below-Casimir data. The threshold MFP is a fitting parameter and found to be $\sim$ 4-7 times of the pitch distance ($p = 1.1 \mu$m).
3.4.2 Seebeck Coefficient \( S \)

Seebeck effect in silicon was briefly introduced in Section 1.2.3. The two contributions: diffusion and phonon drag, have distinct origin in transport phenomena. The diffusion part arises due to non-equilibrium of electron distribution functions with the presence of a temperature gradient. Alternatively, we can look at this phenomenon as a tilted Fermi level. In order to reach equilibrium, carriers move towards the cold side to establish an electric field, which prevents further carrier diffusion. At equilibrium, there is no net movement of carriers, however this established counter electric field is reflected as a voltage macroscopically. This is known as the diffusion part of the Seebeck coefficient. We can derive this effect from Boltzmann Transport Equation (BTE).

Under relaxation time approximation (RTA), BTE can be written as:

\[
\frac{\partial f}{\partial t} + v \nabla f + q \varepsilon \frac{\partial f}{\partial p} = \frac{f_0 - f}{\tau},
\]

where \( f_0, f \) are equilibrium and perturbed carrier distribution functions, \( v, p \) are carrier velocity and momentum, \( q, \varepsilon \) is carrier elementary charge and electric field respectively and \( \tau \) is carrier relaxation time. We can also simplify BTE by assuming quasi-steady state: \( \frac{\partial f}{\partial t} \ll v \nabla f \), and local equilibrium: \( \nabla f \approx \nabla f_0 \). Further, \( \frac{\partial f}{\partial p} \approx \frac{\partial f_0}{\partial p} = \frac{\partial f_0}{\partial E} \frac{\partial E}{\partial p} = v \frac{\partial f_0}{\partial E} \). Now BTE can be rewritten as:

\[
v \left[ \nabla f_0 + q \varepsilon \frac{\partial f_0}{\partial E} \right] = \frac{f_0 - f}{\tau}.
\]

If the spacial variation of carrier distribution is induced by a temperature gradient, \( \nabla f_0 \) can be expressed in terms of \( \nabla T \) as

\[
\frac{\partial f_0}{\partial x} = -\frac{\partial f_0}{\partial E} \frac{E - E_F}{T} \nabla T.
\]

Therefore, combining Eq. 3.16 and Eq. 3.17, the perturbed distribution function is

\[
f = f_0 - \tau v \left[ q \varepsilon - \frac{E - E_F}{T} \nabla T \right] \frac{\partial f_0}{\partial E}.
\]
The current density is defined as:

$$J_x = -\frac{1}{4\pi} \int_0^\infty \int_0^{2\pi} \int_0^\pi fD(E)ev_x \sin \theta d\theta d\phi dE.$$  \hspace{1cm} (3.19)

Since Seebeck effect is the open circuit voltage, we set $J_x$ (Eq. 3.19) to zero. The obtained diffusion part of the Seebeck coefficient is

$$S_d = -\frac{\Delta V}{\Delta T} = -\frac{1}{eT} \left[ \int \frac{\partial f_0}{\partial E} D(E)(E - E_f) \tau dE \right].$$  \hspace{1cm} (3.20)

It is the average energy transported by carriers with respect to Fermi level, which recovers to Eq. 1.3. Note that the relaxation time $\tau$ in both numerator and denominator is energy dependent and the dependence varies with different doping levels. It can be evaluated using Matthiessen’s rule $\tau^{-1} = \sum \tau_i^{-1}$, where $i$ represents phonon, impurity, electron-electron, and plasmon scattering. A simpler approach is to assume a power dependence of mean free path on carrier energy: $\lambda \propto E^r$, where $r$ is characteristic scattering constant [88]. Therefore, Eq. 3.20 can be expressed as:

$$S_d = -\frac{k_B}{e} \left[ \frac{(r + 2)F_{r+1}(\eta)}{(r + 1)F_r(\eta)} - \eta \right],$$  \hspace{1cm} (3.21)

where $\eta = \frac{E_F}{k_BT}$ is the reduced Fermi level, and

$$F_j(\eta) = \int_0^\infty \frac{x^j}{1 + \exp(x - \eta)} dx$$  \hspace{1cm} (3.22)

is the $j$th order Fermi-Dirac integral. The scattering constant $r$ varies between 0 and 2 [89]. $r = 0$ stands for scattering with longitudinal acoustic phonon, $r = 1$ is for optical phonon scattering and $r = 2$ represents the extreme limit for ionic impurity scattering. We also note there is a much simpler form of diffusion Seebeck coefficient: the Mott formula [90], which is a function of effective mass $m^*$ and carrier concentration $n$:

$$S = \frac{8\pi^2 k_B^2}{3\epsilon h} m^* T \left( \frac{\pi}{3n} \right)^{2/3}.$$  \hspace{1cm} (3.23)
Figure 3.27: Measured Seebeck coefficient as a function of temperature for 4 different doping concentrations and their corresponding fitting curves using Eq. 3.21. The values of characteristic scattering constant $r$ is found to be between 0.3-0.7.

However we choose Eq. 3.21 over the Mott formula as the latter is most suitable for degenerately doped semiconductor or metal.

Figure 3.27 plots the measured Seebeck coefficient for 4 different doping concentrations and their corresponding fitting using Eq. 3.21. The fitting procedure is as follows: the reduced Fermi level is implicitly found from $n = \int_0^\infty D(E)f_0(E)dE$ for a given doping concentration at each temperature, it is then plugged into Eq. 3.21 to match the measured values with $r$ as a tuning parameter. During the fitting process, we found the temperature trend is not sensitive to $r$, but the magnitude is. The values of $r$ is between 0.3-0.7 for those samples, in agreement with post-doped porous silicon nanowires [91].

In aforementioned fitting process, we used the diffusion part to fit the total Seebeck as measured. This is not strictly valid as phonon drag has not been included in the model. The phonon drag contribution $S_{ph}$ arises due to momentum transfer from long wavelength phonons to electrons, as if 'dragging' electrons from hot towards cold side. As temperature increases, phonons get randomized by Umklapp scattering before they can transfer
momentum to electrons. As a result, $S_{ph}$ displays a decreasing trend with temperature [92]. The combined total Seebeck coefficient in bulk silicon also exhibits a decreasing trend due to the dominance of $S_{ph}$ for doping levels below $1 \times 10^{19} \text{cm}^{-3}$, above which, it becomes flat [81]. However, none of the measured samples displays such trend. This observation suggests that in those nanostructures, phonon drag is no longer significant. Instead, diffusion part is now the dominant mechanism for Seebeck effect. This is consistent with the reduced total Seebeck coefficient compared to bulk silicon at similar doping level. Figure 3.28 reveals such comparison between nanostructure doped at $8 \times 10^{18} \text{cm}^{-3}$ and bulk silicon at $1 \times 10^{19} \text{cm}^{-3}$.

The difference is significant. What’s more significant, as discussed in previous paragraph, is the disagreement in temperature trend. Clearly difference mechanisms are present between nanostructure and bulk silicon. From Eq. 3.21, we know similar diffusion contribution exists in both structures. Even thought dominant scattering process maybe different (in fact, electron boundary scattering is insignificant at this length scale), the expected impact to Seebeck effect is small. Not to mention that the disagreement in temperature
trend cannot be explained by different scattering processes. Therefore one probable explanation is that the Phonon drag which exists in bulk silicon, is now quenched in nanostructure. And by taking the difference between the two sets of data in Figure 3.28, we can extract $S_{ph}$ in bulk silicon doped at $\sim 1\times10^{19}\text{cm}^{-3}$.

To predict $S_{ph}$ in silicon requires solving the coupled BTE for electrons and phonons, which seemingly is not a trivial task. However it is illustrative to first look at the individual contribution from phonons and electrons. From phonon’s perspective, the relaxation paths include scattering processes due to Umklapp, impurity (mass difference), surface boundary and electrons. Amongst those, phonon-electron scattering is the driving force for $S_{ph}$. This interaction has already been discussed by Eq. 3.14 in previous section of thermal conductivity. The strength of phonon-electron interaction relative to the overall phonon scattering is a measure of how big $S_{ph}$ is. Therefore we can estimate $S_{ph}$ from:

$$S_{ph} \propto \frac{1}{n} \sum_{\lambda, q} \frac{q^2}{q^2 \sum \tau_{p-e}^{-1}},$$

(3.24)

where $q$ is phonon wave number, $\tau_{p-e}$ (Eq. 3.14) is phonon scattering due to electrons and $\sum \tau_p$ is the total phonon scattering. These expressions are $q$ dependent. This is particularly important to distinguish between the long wavelength phonons that contributes to the interaction with electrons, and the short wavelength phonons that conducts most of the heat. Short wavelength, high frequency phonons does not participate with electron interaction, as their energy is too high to satisfy the energy and momentum conservation requirement (as in Eq. 3.13).

Now, let’s consider the effect of boundary scattering toward phonon drag. As structure gets smaller, phonons start to interact with surface boundaries. It is generally accepted that phonon scattering with surface boundary is frequency independent, which is often referred as gray model:

$$\tau_b = \frac{v}{F d'},$$

(3.25)

where $v$ is phonon velocity, $d$ is limiting dimension and $F$ is geometric factor. Figure 3.29 compares the frequency dependent phonon scattering rates
Figure 3.29: Spectral comparison of phonon scattering due to different interactions. Note the distinctive low-frequency dominance in electron-phonon scattering.

...in silicon at 300 K, which includes Umklapp, mass difference, surface and electron scattering.

As evident in Figure 3.29, boundary scattering is the most dominant mechanism for low frequency phonons while Umklapp and mass difference scattering dominate in high frequency regime. The low frequency phonons are also responsible for most of the interaction with electrons, hence the phonon drag in Seebeck. As a result, low frequency long wavelength phonons get randomized by surfaces before they can transfer momentum to electrons. Depending on boundary scattering strength, phonon drag may completely vanish for smaller feature sizes. Figure 3.30 reveals the effect from reducing limiting dimension to $S_{ph}$. This plot is generated for carrier concentration at $1 \times 10^{19} \text{ cm}^{-3}$ and other carrier concentrations have similar behavior.

The influence from surface boundary scattering starts to become relevant when limiting dimension becomes smaller than 10 $\mu$m. As limiting dimension continues to decrease, $S_{ph}$ encounters a sharp decline around $\mu$m length scale, and is completely vanished below 100 nm. From this aspect, it is justified for us to fit our measurement data using only the diffusion component of Seebeck effect as in Figure 3.27.
Figure 3.30: Normalized phonon drag as a function of limiting dimensions calculated from Eq. 3.24. $S_{ph}$ starts to decrease as limiting dimension becomes smaller than 10 µm and completely vanished below 100 nm.

We can also look at phonon drag from electron’s perspective. When receiving momentum from phonons, electrons need a time window so that no simultaneous momentum relaxation toward lattice, impurities etc. Electron momentum relaxation towards lattice (phonons) could be viewed as emission in phonon-electron interaction. However, when dopant density becomes significantly large in silicon, electrons could quickly lost momentum (gained from phonons) through ionic impurity scattering. To estimated the effect of increasing dopant density, we can plot the relative of strength of electron scattering due to phonons with respect to total electron scattering rates:

$$S_{ph} \propto \frac{1}{n} \sum_{E} \frac{v_{x}^{2}}{v^{2}} \frac{\tau_{e-p}^{-1}}{\tau_{e}^{-1}}. \quad (3.26)$$

We note that this expression is not rigorously derived from BTE, and it may not fully represent the effect of dopant density in phonon drag. However, it is still illustrative to see qualitatively what is the relative strength of phonon-electron scattering. Figure 3.31 plots the normalized $S_{ph}$ against doping levels in silicon at 300 K.

As shown in Figure 3.31, $S_{ph}$ is insensitive to doping level below $1 \times 10^{16} \text{cm}^{-3}$,
Figure 3.31: Normalized phonon drag as a function of limiting dimensions calculated from Eq. 3.26. $S_{ph}$ starts to decrease as doping level reaches $1 \times 10^{16} \text{cm}^{-3}$. At $1 \times 10^{19} \text{cm}^{-3}$, about 20% of $S_{ph}$ still exists in bulk silicon at 300 K.

where phonon electron scattering dominates in silicon. However, the relative strength of phonon electron scattering gradually decrease and at $1 \times 10^{19} \text{cm}^{-3}$, $S_{ph}$ drops to roughly 20% of its original value at low doping. This trend is somewhat contradictory to current understanding of phonon drag, which states that $S_{ph}$ is negligible at doping concentration at the order of $1 \times 10^{19} \text{cm}^{-3}$. In fact, at this doping level, the phonon drag component in bulk silicon is more than 100 $\mu$V/K, which is comparable to diffusion contribution.

Back to the introduction section of this dissertation, when assessing silicon’s potential as thermoelectric material, one favorable argument, based on the dissimilarity of MFPs of phonons and electrons, is that silicon nanostructure could decrease thermal conductivity while maintain electrical properties. It certainly needs a reassessment. While it is true that electrical conductivity is minimally affected, Seebeck coefficient takes a big impact, as almost the entirety of phonon drag, which contributes a sensible portion of $S$ in bulk, is quenched due to enhanced boundary scattering of long wavelength phonons.

Sadhu [32] derived the formulation from coupled BTE with a phonon MFP
Figure 3.32: Extracted values of phonon drag from Figure 3.28. The dashed fitting curve is calculated from Eq. 3.27 with fitting parameter deformation potential $D_A = 5.5$ eV.

spectrum as was able to capture the temperature dependent $S_{ph}$ from 50 K to 300 K. The expression is:

$$ eTS_{ph} = \frac{\int_0^\infty \tau ev^2_x D(E) f'_0 dE}{\int_0^\infty \tau ev^2_x D(E) f'_0 dE} \frac{1}{2k^3} \int_0^{2ku_0} \frac{C(\omega) d\omega \Lambda_{ep}^{-1}}{f_0(\frac{\omega}{2u_0}) \Lambda_p^{-1}} $$

(3.27)

where $k$ is electron wavevector, $u_0$ is longitudinal phonon velocity, $C(\omega) = \hbar \omega \langle dN_0/dT \rangle (\omega^2/u_0^3)$ is specific heat per frequency. The only fitting parameter is the deformation potential in electron-phonon scattering. Figure 3.32 plots the extracted phonon drag component by taking the difference between Seebeck coefficient of bulk and thin film silicon in Figure 3.28. The fitting curve is calculated from Eq. 3.27 and the fitting parameter deformation potential $D_A$ is found to be 5.5 eV. The value of $D_A$ is smaller than the usual value of 9 eV but they are at the same order of magnitude. More importantly, the temperature trend is well captured by this model.
Figure 3.33: Measured power factor of periodic porous silicon (open squares) as a function of carrier concentration at 300 K. The solid red and blue curves are theoretical calculations for bulk and silicon nanostructure respectively. The only difference is the exclusion of phonon drag in $S$ of nanostructure.

3.4.3 Thermoelectric Power Factor and $ZT$

Now we discuss the practical implications of our experimental results on silicon nanostructures. The intention of using silicon nanostucture is to reduce thermal conductivity without affecting significantly electrical properties. Initially, the electrical property refers to electrical conductivity, given the smaller mean free path. In our experiment, we observed minimum impact to $\sigma$ from boundary scattering, charge depletion an etc with a limiting dimension on the order of $\sim 100$ nm. However, the Seebeck coefficient is unexpectedly suppressed due to phonon drag quenching. Although phonon drag part is not the dominant part in $S$, the impact to overall power factor $S^2\sigma$ is amplified by the quadratic dependence of $S$.

Figure 3.33 plots the measured power factor (blue open squares) as a function of carrier concentrations. For periodic porous structure, effective electrical conductivity is converted back to material conductivity $\sigma_0$ using the effective medium theory. The red and green curves are theoretical calculations for bulk and nanostructured silicon. The only difference is the exclusion
of phonon drag in $S$ of nanostructure.

In our experiment the best power factor is achieved at $3.6 \times 10^{19}$ cm$^{-3}$, which is in line with bulk silicon. The optimal carrier concentration for power factor depends on electronic band structure. At such dimensions, similar band structure is expected for nanostructure.

At $3.6 \times 10^{19}$ cm$^{-3}$, the measured power factor is 1.89 mW/mK$^2$, which is significantly lower than predicted bulk value: 3.23 mW/mK$^2$. The reduction represents 41% of the bulk power factor, which is attributed to the vanish of phonon drag.

Figure 3.34 plots measured $ZT$ as a function of temperature between 300 K and 420 K. Amongst all the samples, one have all three thermoelectric properties $S$, $\sigma$ and $k$ measured, which is shown as blue circles. The green squares represent two separate measurements of thermal and electrical properties of two samples on one single chip. At 300 K, the best measured $ZT$ is about 0.036 for the sample with 38% porosity. Compared with optimally doped bulk silicon, this value represents a 4-fold enhancement. The reduc-
Figure 3.35: Theoretical largest thermoelectric figure of merit $ZT$, minimum thermal conductivity $k$ and power factor as a function of carrier concentration in silicon at 300 K. Total thermal conductivity consists of electronic and lattice contribution. The latter is taken as the amorphous limit of silicon.

tion in thermal conductivity is estimated to have a 10-fold increase in $ZT$, however, a majority portion of the enhancement is offset by the vanish of phonon drag in $S$.

The best $ZT$ reported for periodic porous silicon is 0.4 [10] at 300 K, which is 10 times better than our measurement. Those samples have a limiting dimension on the order of 20 nm, and it is surprising that electrical properties were not affected significantly. A more recent measurement [12] reports $ZT$ of 0.04 at 300 K, which is close to our value. However, there is a distinct difference: our measurement falls in a regime where electrical conductivity is preserved with modest reduction in thermal conductivity, whereas in Ref. [12], thermal conductivity is drastically reduced and so is electrical conductivity but to a lesser extend.

This brings us to the question: what is the largest possible $ZT$ for silicon nanostructure? We assume bulk-like electrical conductivity and Seebeck coefficient without phonon drag. The resulting power factor is already shown
in Figure 3.33. For thermal conductivity, we assume the lattice contribution \(k_l\) to be the amorphous limit \(k_a\) [93] and add the electronic contribution according to Wiedemann-Franz law. These two parts and the total thermal conductivity are plotted in the central panel of Figure 3.35. Finally, \(ZT\) is plotted in the upper panel. The optimal doping is shifted slightly to left due to the dominance of electronic thermal conductivity at higher doping. The projected \(ZT\) is about 0.47 at 300 K.

We point out that this maximum limit in \(ZT\) is overly optimistic due to the unlikely coexistence of amorphous-like thermal conductivity and bulk-like electron mobility. Previous studies show fine grain boundary is better than surface boundary at reducing thermal conductivity (coherence effect) and at the same time preserving electrical conductivity (tunneling effect). Calculations show \(ZT \sim 0.15\) at 300 K and \(\sim 0.6\) at 600 K are achievable with both limiting dimensions of surface and grain boundary \(\leq 10\) nm.
CHAPTER 4

COHERENT PHONON-GRAIN
BOUNDARY SCATTERING IN SILICON
INVERSE OPALS

4.1 Introduction

Inverse opals [94] are a class of 3D periodic structure [95,96] where material is deposited in the interstices of a colloidal crystal followed by removal of the original template. As mentioned in Section 2.2.2, they are of great interest as functional materials in applications like optoelectronics, battery electrode as well as thermoelectrics.

The inverse opal geometry modifies flow fields such that the effective conductivity of an inverse opal thin-film is different from the intrinsic conductivity. However, the ratio of the effective electrical to thermal conductivity is the same as the ratio of the intrinsic material conductivities, since electrical and thermal flow fields remain similar inside an inverse opal [37]. Thus, the geometry in itself does not affect the figure of merit in the continuum regime.

The overall resistance posed by the structure does depend on geometry as emphasized above. The relation between the effective conductivity and the intrinsic conductivity can deviate substantially from the effective medium.

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1This chapter has in part appeared in Jun Ma, B.R. Parajuli, M.G. Ghossoub, A. Mihi, J. Sadhu, P.V. Braun, and S. Sinha, “Coherent Phonon-Grain Boundary Scattering In Silicon Inverse Opals”, Nano Letters vol. 13 (2), pp 618-624 (2013). Copyright 2013, American Chemical Society. Author contribution: S.S. and P.V.B. directed the research, B.R.P. and A.M. provided inverse opal samples, J.M. fabricated measurement device, conducted experiment and performed data analysis, J.M., M.G.G. and J.S. performed XRD and TEM characterization, J.M. and S.S. wrote the manuscript, all authors reviewed the manuscript.

The measurement details and part of the preliminary results have been published previously in author’s Master thesis: Jun Ma, “Thermoelectric Properties of Polysilicon Inverse Opals”, 2012, University of Illinois at Urbana-Champaign.

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theory as discussed in Section 2.1.1. Typical inverse opals made from self-assembled oxide spheres, possess shell thickness, $d$ in the range $\sim 15$–$35$ nm and inner diameters, $R_{\text{inner}}$ in the range $\sim 100$–$300$ nm [96]. The relationship between the inner diameter of the sphere and the shell thickness is well defined if the pores in the opal structure are filled to the maximum at 86% [97]. The FCC opal has a filling factor of 74%, and the maximum filling factor of the inverse opal is $86% \times (1-0.74) \approx 22%$. Using this figure, $d$ is approximately equal to 12% of $R_{\text{inner}}$ [97] if we account for the presence of these interconnecting holes. The porosity is well exceeding 0.75 and we cannot employ the MG model with spherical voids to estimate the effective conductivities. We use instead the relations provided by a boundary integral solution to the flow fields [37]. At the theoretical minimum porosity of $\sim 78\%$, the effective conductivity is $\sim 11.5\%$ of the intrinsic material conductivity.

In this chapter, we will present our experimental study on the thermal transport in silicon inverse opals and discuss in details the implication from low temperature data.

4.2 Sample Fabrication and Characterization

The current literature describes the fabrication of silicon inverse opals in detail [68, 98]. Figure 4.1 depicts the fabrication scheme chosen for this work. We employed the Stober method [99] followed by several regrowth cycles to synthesize silica spheres ranging in diameter from 300-640 nm. Prior to crystal growth, we heat-treated the spheres for 6 hours at 600 °C to avoid shrinkage that potentially leads to cracking of the opal structure during post-processing at elevated temperatures [100]. Using a modified vertical deposition method [101] that employs a temperature gradient [98], we deposited colloidal crystal films on a single side polished Si substrate (Figure 4.1A). After a Piranha clean, substrates were placed at a 20° angle in a 20 mL scintillation vial (Fisher) with 4 g of colloidal dispersion (2-3% w/w in ethanol). The vials were left in an incubator (Fisher, Isotemp 125D) at 42-45 °C overnight. We noticed that the appropriate temperature window used to grow high quality opals was small and occasionally needed to be experimentally adjusted. Reflection and transmission spectroscopy along with SEM
provided measures of the thickness and quality of the samples. We only selected high quality (closely-packed) templates with 5-8 opal layers for further processing. Figure 4.2A shows an SEM of a typical sample.

For such templates, we deposited a thin conformal film of high-quality, low-roughness amorphous Si around the spheres (Figure 4.1B) using a static CVD system with disilane (Si$_2$H$_6$, 98%, Gelest) as a silicon source at 350 °C (50 mbarr, heating rate 8 °C min$^{-1}$). We controlled the deposition time to make sure that the pores in the opal template were filled to a maximum.22 Pores in the underlying opal structure are filled to the maximum at 86% once the silicon overlayer starts forming during the fabrication described above.23 The shell thickness is approximately equal to 6% of the diameter of silica in this case [97]. Scanning electron microscopy (SEM) provided additional confirmation of this feature size. Samples were annealed in a tube furnace at 1000 °C for 10 hours under forming gas to recrystallize the amorphous silicon. We used reactive ion etching (1 min, 70 W, gasses SF$_6$ and O$_2$ 20 sccm, 50 mTorr chamber pressure) to open a $1 \times 2$ mm$^2$ window defined by a Kapton film (Figure 4.1C). This window allows the creation of an inter-penetrating network of oxide within the opal template by exposing the silica spheres at the surface when immersed in an ethanol solution of 5% hydrofluoric acid for 25-30 mins. Selectively etching only a small region of the sample prevented cracking and sample lift-off. The opal template was completely etched away leaving the silicon inverse opal structure (Figure 4.1D). Figure 4.2B shows the SEM of a typical sample after RIE and HF etching.

The diameter of silica spheres, $D$ controls two feature sizes in the inverse opal that directly affect phonon heat conduction: The thickness of the silicon shell, $d$, that controls the phonon mean free path for surface scattering and the nominal size of the grains, $l$, that controls phonon grain boundary scattering. We have discussed measurement of the shell thickness above and now discuss measurements of the grain size. We anticipate grains to be limited in size by the thickness of the shell [102]. Transmission electron microscopy (TEM) confirms polycrystalline nature and also reveals atomic scale surface roughness but can only image the grain over a small region. Figure 4.2C and 4.2D show TEMs of a typical sample.

We employed X-ray diffraction (XRD) to measure the average grain size
Figure 4.1: Overview of the silicon inverse opal structure fabrication scheme. (A) Three-dimensional fcc silica opal template. (B) Silica opal coated with a thin layer of a-Si via CVD. (C) Annealed sample with RIE to expose silica. (D) Silicon inverse structure after etching the silica template.
across the entire depth of the sample over spot sizes 1mm in diameter. A $2\theta - \omega$ scan yields the average crystallite size along the height of the inverse opal layer. The inset of Figure 4.3 shows the XRD data for a sample fabricated using 420 nm silica spheres. Figure 4.3 further plots the average grain size for the measured inverse opals as a function of the diameter of the silica spheres used in the fabrication. The systematic trend of the data confirms the hypothesis that grain size is essentially limited by the thickness of the silicon shell. As discussed above, the diameter of the silica spheres directly controls the thickness of the silicon shell. We find the average grain size to decrease from 36 nm (with $D = 640$ nm) to 20 nm (with $D = 300$ nm). As the diameter of the spheres and consequently the thickness of the silicon shell decreases, the distribution in grain sizes also becomes narrower.
Figure 4.3: The average grain size from XRD measurements. Inset: XRD profile of a typical silicon inverse opal sample. We average the grain size over three orientations, (111), (220), and (311).

4.3 Thermal Conductivity Measurement

Our samples effectively possess a thin-film geometry with thicknesses in the range 2-6 $\mu$m. The frequency domain $3\omega$ method [103] can readily measure the thermal conductivity of such samples. Previous work [104,105] describes the $3\omega$ method in detail. In brief, a sinusoidal current at a frequency $\omega$ through a metallic heater sets up an oscillatory temperature rise, $\Delta T$ at the harmonic frequency $2\omega$. This results in a voltage across the metal line oscillating at frequency $3\omega$. Measurement of the $3\omega$ voltage via a lock-in amplifier provides $\Delta T$. Comparing the measured $\Delta T$ with a model of multi-layer heat diffusion [106] enables the extraction of thermal conductivity of the sample.

We next discuss the design of $3\omega$ measurements for our samples.

Based on previous measurements of thin silicon [107] and polysilicon films [48], we expect the effective room temperature thermal conductivity of the films to be rather small at 1 W/mK on account of the large porosities. Assuming a thermal conductivity of 1 W/mK and a bulk-like volumetric heat capacity scaled appropriately by the porosity, the expected thermal diffusivity, $\alpha$ is $\sim 3 \times 10^{-2}$ cm$^2$/s at room temperature. For the typical frequency
range of 10-1000 Hz used in $3\omega$ measurements, we estimated the thermal penetration depth to be 30-300 $\mu$m at room temperature. This is much larger than the thickness of the inverse opal layer and allows the $3\omega$ measurement to probe the entire thickness of the thin film with the substrate underneath acting as the reference. Heat flow across the sample during the measurement is essentially one-dimensional when the width of the heater is chosen to be greater than the thickness of the sample [104]. This further simplifies thermal conductivity extraction.

The preparation of samples for the $3\omega$ measurements proceeded as follows. We employed plasma-enhanced chemical vapor deposition (PECVD) to deposit a 100 nm thick silicon dioxide layer on the sample, and patterned a 300 nm thick, 50 $\mu$m wide Au heater line through a shadow mask. The heater is thick enough to maintain physical contact with the wavy substrate underneath. The large width compared to the sample thickness ensures one-dimensional heat flow across the sample, as discussed above. Post-measurement cross-sectional SEMs confirmed continuous physical contact across all interfaces.

All layers and interfaces present in the $3\omega$ sample described above contribute to $\Delta T$ but the thermal impedance posed by the inverse opal layer dominates over the rest. The thermal diffusivity of the bulk Si substrate is typically more than two orders of magnitude larger than that of the inverse opal layer. At 300 K, we expect the inverse opal layer to dominate and contribute more than 80% of the temperature rise at the heater. Based on previously measured values [108], we estimate impedances from interfaces and the oxide to be small. At 300 K, for example, these contribute <3% to the total temperature rise. Calibration for the measurement involves measurement of the electrical resistance of the heater line at low currents (250 nA). We use the Bloch-Grüneisen formula [109] to fit the electrical resistance of the heater line in the temperature range of 15-400 K. This serves as the calibration for subsequent electrical resistance based thermometry. Differentiating the fit yields the temperature coefficient of resistance, $dR/dT$ of the heater.

During the measurements, we observed a linear relation between $\Delta T$ and the logarithm of heater frequency for all temperatures at low frequencies,
Figure 4.4: $\Delta T$ as a function of frequency at low temperature. Open circles represent measurement data and fitted curves are derived from a multi-layer model [106].

confirming an essentially one-dimensional heat flow across the inverse opal films. In certain cases as shown in Figure 4.4 for $\Delta T$ at low temperature, we see a “tail” at higher frequencies, which indicates that the penetration depth is now comparable to inverse opal layer thickness. We checked for errors in the one-dimensional approximation by comparing fitting the temperature rise with a two-dimensional multilayer heat diffusion model (as in Figure 4.4) but found the discrepancy in extracted thermal conductivities to be smaller than 0.5%. We note that during the course of a complete temperature sweep (30-400 K), $\Delta T$ was always smaller than 2 K for all samples except for the smallest sample at 30 K. In the latter case, $\Delta T$ was 4 K. Since we assume the base temperature of the sample as the temperature of the cryostat, we expect the error in this assumption to be less than 2 K except as noted above. We could not obtain reliable data below 30 K since the resistivity of Au loses sensitivity to temperature.
4.4 Results and Discussion

Figure 4.5 shows the measured effective thermal conductivities (right axis) of four inverse opal samples\(^2\). The thickness of the silicon shell and the average grain size in each sample are indicated. All samples possess a relatively low thermal conductivity (\(\sim 1\) W/mK at room temperature) owing to the large porosity and bending of heat flow lines inside the structure as discussed previously. Using numerical solutions obtained in Ref. [37], we convert the effective thermal conductivities to the material thermal conductivities. The latter are shown on the left axis. The thermal conductivity of previously measured undoped LPCVD polysilicon films with 1-4 \(\mu\)m thickness [110] ranges between 15-55 W/mK at 300 K for grain sizes in the range 190-550 nm. Thermal conductivity modeling of this data set revealed that thermal conductivity scales approximately proportional to the grain size. The material thermal conductivities of silicon inverse opals are lower than those of the previous LPCVD thin-films since the grain size in our samples are nearly an order of magnitude smaller than previous samples. However, in contrast to LPCVD thin films, the material thermal conductivities of inverse opals at 300 K do not scale in direct proportion to the grain size when compared with the previously measured values or between our samples. A direct scaling of thermal conductivity with grain size would yield material thermal conductivities of inverse opals in the range 2.8-5.1 W/mK at 300K. The measured values are approximately 50% larger. Thus, a grain size dependent mean free path does not explain the thermal conductivity of inverse opals. We now turn to the low temperature data for more insight.

The variation of thermal conductivity with temperature at low temperatures (prior to the strong onset of Umklapp scattering) is indicative of the frequency dependence of the dominant phonon scattering mechanism. Applying results from the kinetic theory, the lattice thermal conductivity of a three-dimensional phonon gas is [15]

\[
k = \frac{1}{3} \sum_{\lambda,j} C_{\lambda,j} \Lambda,
\]

\(^2\)After fabrication, each sample was cleaved into two pieces: one for XRD and one for thermal measurement.

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where $j$ represents different phonon modes. The volumetric heat capacity, $C$, the phonon group velocity, $v$, and the phonon mean free path, $\Lambda$ are frequency dependent quantities appearing in the conductivity summation. At low temperatures, if the surface or alternately the grain boundary dominates phonon scattering, the mean free path typically remains independent of the phonon frequency. Thus, the temperature dependence of thermal conductivity follows the well-known $\sim T^3$ dependence of the heat capacity. The thermal conductivity of LPCVD polysilicon films follows such temperature dependence at low temperatures indicating a frequency-independent mean free path arising from grain boundary scattering.

The conductivity data in Figure 4.5, however, varies as $k \sim T^{1.8}$ at low temperatures. We expect the material in the sample to possess a heat capacity similar to the bulk since lattice dynamics calculations clearly show phonon dispersion and density of states to remain unaltered at these dimensions [16]. In silicon inverse opals, surface scattering is equally important as grain boundary scattering since the feature sizes are similar. However, a frequency dependence arising from surface scattering is unlikely since TEM
images show atomic scale roughness at the surfaces. In this case, surface scattering should be consistent with the Casimir model \([17, 18]\) and independent of frequency. Thus, the weaker than \(\sim T^3\) temperature trend of the data is puzzling at first glance. Using detailed phonon scattering theory below, we show that this trend plausibly originates from coherence of the reflected phonon in the inter-grain region. This yields a frequency dependence in the grain boundary scattering rate that results in a weaker than dependence in the thermal conductivity data.

In equating the phonon mean free path with the grain size, there is an implicit assumption that phonons are randomly scattered at all grain boundaries. This is not strictly valid at low temperatures. Phonons scatter near a grain boundary due to change in orientation of crystal planes as well as disorder in the inter-grain region. In a perturbative approach, both induce a perturbation in the wave velocity, \(\Delta v\). The change in wave velocity leads to back-scattering from mode \(q\) to \(q'\) whose rate is

\[
\tau_g^{-1}(q) = \frac{V}{(2\pi)^3} (\rho \omega)^{-2} \sum_j \oint v_g^{-1} |2M(q, q')|^2 dS',
\]

(4.2)

where \(V\) is the volume of a crystal containing one boundary, \(\rho\) is the density, \(v_g\) is the phonon velocity, \(dS\) is the surface element, \(j\) is polarization. The perturbation element \(M(q, q')\) is

\[
M(q, q') = V^{-1} \rho \omega^2 \int d\mathbf{r} \delta v(\mathbf{r}) e^{iQ \cdot \mathbf{r}} (\epsilon \cdot \epsilon')(\epsilon \cdot \epsilon'),
\]

(4.3)

where \(\epsilon, \epsilon'\) are unit vectors along the polarization directions, and \(Q=q'-q\). Klemens \([50]\) showed that randomized scattering at a tilt boundary gives rise to a frequency independent scattering rate

\[
\tau_g^{-1} = \frac{2}{3} (v/l) (\Delta v/v)^2,
\]

(4.4)

where \(l\) is average grain size, \(\Delta v\) is the change in velocity at the tilt boundary. The magnitude of the rate is typically small since \(\Delta v/v \sim o(0.1)\). Similar randomized scattering in the inter-grain region with greater disorder leads to much stronger scattering since \(\Delta v/v \sim 1\) in this case. However, for scattering to be incoherent, the two boundaries of the inter-grain region should be far
apart compared to the phonon wavelength. This suggests a critical frequency, \( \omega_{cr} \simeq v/t \), below which scattering is increasingly coherent. Here \( t \) is the thickness of the inter-grain region.

For frequencies lower than this critical frequency, the two boundaries scatter phonons coherently. This is especially likely at low temperatures since \( t \) is typically \( \sim \AA \) scale and much smaller than phonon wavelengths. The scattering rate in this case has a quadratic frequency dependence [50],

\[
\tau_g^{-1} = \frac{3 \omega^2 t^2}{4 v t} (\Delta v/v)^2,
\]

where \( \Delta v \) is now the change in velocity due to inter-grain region. We show below that such frequency dependence explains the weaker than \( \sim T^3 \) dependence in the thermal conductivity of inverse opals.

We also point out recent work on nanocrystalline Si [49] that suggests linear frequency dependence in the grain boundary scattering rate. The expression for the scattering rate in this case is proportional to the phonon transmission coefficient of the grain boundary. Atomistic simulations reveal that the transmission coefficient itself can have strong frequency dependence, in which case the frequency dependence of the scattering rate would be stronger than the linear dependence assumed in the work. To proceed, we fit the thermal conductivity data using the \( \sim \omega^0, \sim \omega^1, \sim \omega^2 \) frequency dependencies.
respectively in the grain boundary scattering rate discussed above.

To obtain the fit, we follow an approach to modeling thermal conductivity similar to those proposed by Callaway [47] and Holland [111] but include a modification proposed by Mingo [16]. Mingo suggests the use of a cut off frequency, \( \omega_c \), smaller than the Debye frequency, \( \omega_D \) in fitting the experimental thermal conductivity of silicon nanostructures. This approach accounts for the difference in the phonon dispersion relation between the Holland model and more accurate lattice dynamics calculations. Here, we follow Mingo’s approach and treat \( \omega_c \) as a fitting parameter in subsequent modeling. We note that the fit is not overly sensitive to the particular value of \( \omega_c \) since Umklapp scattering strongly reduces the contribution of high frequency phonons to heat conduction much before the cut-off frequency [112].

Assuming a linear dispersion relation and treating all polarizations equivalently, the expression for thermal conductivity is

\[
k = \frac{1}{2\pi^2 k_B T^2 v} \int_0^{\omega_c} \frac{(\hbar \omega)^2 \omega^2 e^{\hbar \omega/k_B T}}{[e^{\hbar \omega/k_B T} - 1]^2} \tau(\omega) d\omega, \quad (4.6)
\]

where \( v = 6.4 \times 10^3 \) m/s is now the average phonon propagation speed [111], \( k_B \) is the Boltzmann constant and \( \hbar \) is the reduced Planck’s constant. The frequency dependent phonon relaxation time \( \tau(\omega) \) can be calculated using Matthiessen’s rule, assuming scattering due to isotopes, Umklapp processes, surfaces and grain boundaries to be independent. The expressions and values of constants have been presented in Section 2.1.3.

Surface scattering in an inverse opal is complicated due to the complex geometry. A rigorous but tedious approach involves solving the phonon Boltzmann equation in the exact geometry. However, the main effect of the lattice geometry is the macroscopic bending of heat flux lines rather than microscopic effects on phonon transport, due to the relatively large curvatures involved. Further, grain boundaries likely randomize phonon scattering and remove any geometrical effect of the lattice in surface scattering. With this in mind, we adopt a simpler approach in modeling surface scattering. We assume scattering from the surfaces of the thin segments of the inverse opal to be the same as scattering from the surface of a thin film. Using Casimir’s approach, we obtain \( \tau_b^{-1} = v/(Fd) \) where \( F = 4 \) for a thin-film geometry [113].
Figure 4.7: The material thermal conductivities of inverse opals vary as $\sim T^{1.8}$ at low temperatures. Quadratic frequency dependence in the phonon grain boundary scattering rate yields excellent agreement with data. The solid curves use $\sim \omega^2$ dependent grain boundary scattering rate while the dashed and dotted curves use $\sim \omega^1$ and $\sim \omega^0$ dependent rates. The $\sim \omega^2$ dependence arises due to coherent scattering in the intergrain region.

We show below that this approach leads to excellent fits for all samples, validating our simplifying assumptions. The scattering rates are plotted in Figure 2.2 in Chapter 2.

Referring back to Figure 4.5, all three models for grain boundary scattering fit the data reasonably well at temperature above 200 K. Figure 4.5 only shows the fit obtained using the $\sim \omega^2$ frequency dependent model but the $\sim \omega^0$, $\sim \omega^1$ models fit the data equally well near room temperature. However, the low temperature behavior is significantly different. Figure 4.7 shows the low temperature data with error bars and includes the best fits from the $\sim \omega^0$, $\sim \omega^1$, $\sim \omega^2$ scattering rates. We find that only the $\sim \omega^2$ dependent rate corresponding to coherent scattering in the inter-grain region, is able to fit the data reasonably well at the lowest temperatures. There is a systematic trend in the agreement of the other models with the data. Predictions from the frequency independent model increasingly diverge from the data below temperatures of $\sim 200$ K whereas predictions from the $\sim \omega^1$ model increasingly diverge from the data below $\sim 140$ K. Only the $\sim \omega^2$ model
fits the data down to 30 K. Further, the values of the inter-grain thickness obtained from the best fits range between 1.8-2.2 Å, consistent with values calculated using molecular dynamics of bulk silicon for grain boundaries of different energies [114,115]. In fact, the frequency dependence of the phonon reflection coefficient calculated from these simulations follows $\sim \omega^{2.3-2.5}$ approximately consistent with the proposed model. The excellent agreement of the data with the coherent model and the agreement of the frequency dependency in the model with atomistic calculations, strongly suggest that grain boundary scattering is indeed coherent in silicon inverse opals at low temperatures. The reason behind this is not clear at present. An obvious hypothesis is that grain boundaries in silicon inverse opals possess relatively lower disorder and/or are thinner compared to bulk or thin film polysilicon. In either case, this enables coherence in phonon reflections from the inter-grain region at low temperatures.

4.5 Conclusion

In conclusion, thermal conductivity measurements on silicon inverse opals show effective thermal conductivities $\lesssim 1$ W/mK and material thermal conductivities $\lesssim 10$ W/mK at room temperature. The relatively low thermal conductivities are significant in photonic applications where even relatively small absorption can cause significant temperature rise. In exploring phonon transport in these structures, we find that frequency-dependent, coherent phonon grain boundary scattering explains the data across the temperature range of the measurement down to 30 K. Compared to previous measurements, inverse opals provide access to more uniform grains across the entire sample since grain growth is restricted by the thickness of the silicon shell. On the basis of the thermal conductivity analysis, we hypothesize that the intergrain region is thinner and possesses lesser disorder than typical polysilicon films. This is likely the reason for the clear frequency dependence in our data at low temperatures that is not observed in previous measurements. Assuming that inverse opals can be heavily doped similar to bulk polysilicon, these materials become interesting for thermoelectric energy conversion at high temperatures. Theoretical calculations [31] show $ZT \sim 0.6$ at 600
K, providing impetus for future experiments. This work provides thermal conductivity data useful in technological applications of inverse opals and insight into the physics of phonon heat conduction in these structures.
CHAPTER 5

CONCLUSION AND FUTURE WORK

This dissertation investigates the electrical and thermal transport in periodic holey silicon nanostructure. In 2-D periodic holey structure, we focus on a simultaneous measurement of all three material properties, which has rarely been realized previously for silicon nanostructure. Using a self-heating $3\omega$ method, we are able to measure the thermal conductivity of 2-D holey silicon which only requires the sample portion to be suspended, eliminating complexity of previously reported micro-fabricated devices. We also implemented frequency domain Seebeck measurement on the same device. Our technique demonstrated a complete $ZT$ measurement on silicon nanostructure. In 3-D periodic structure, silicon inverse opals, phonon transport is largely affected by the removal of materials (high porosity) in continuum regime. After accounting for the porosity effect, we found the phonon mean free path is limited by grain boundaries. At low temperature, the unusual power dependence on temperature reveals possible coherent scattering by the intergrain region. In this chapter, we will summarize our findings and briefly discuss the future direction for silicon based thermoelectric application.

Electrical measurement on 2-D periodic holey silicon shows unaffected electrical conductivity for limiting dimension down to 120 nm. This is attributed to the smaller mean free path of electrons at room temperature. In addition, it is found the Seebeck coefficient becomes smaller than bulk silicon at similar doping concentration. While it is hard to argue the change in diffusion part, we hypothesize quenched phonon drag is the reason behind the reduction in $S$. In silicon nanostructure, long wavelength phonons are randomized by boundary scattering before momentum transfer to electrons. This hypothesis is partially validated by the temperature trend in our Seebeck data, which clearly shows the dominance of diffusion contribution. We extracted the phonon drag component by comparing our measurement with reported
bulk $S$. The extracted $S_{ph}$ can be fitted by a solution to the BTE with coupled electron and phonon transport. The excellent agreement in temperature trend also supports our hypothesis.

However, the quenched phonon drag has a negative implication toward thermoelectric application. At optimal doping concentration ($\sim 4 \times 10^{19}$ cm$^{-3}$), phonon drag contributes $\sim 25\%$ of total Seebeck coefficient. Excluding phonon drag results a 40\% reduction in power factor. Even if we assume the amorphous limit of the lattice thermal conductivity, $ZT$ at 300 K is $\sim 0.47$ at best.

As for thermal conductivity measurement, we demonstrated effective reduction using periodic holey structure. We also found thermal conductivity is below the corresponding Casimir limit if the neck distance is taken as limiting dimension. The exact reason is unclear, however, similar phenomena have also been observed in other measurements [12,14]. Due to the constraint in fabrication, we were not able to achieve structures with limiting dimension less than 120 nm. The overall reduction in material thermal conductivity is about 10 times from bulk silicon.

Amongst all samples, the best thermoelectric figure of merit $ZT$ for that sample is 0.036 at room temperature. While the reported highest $ZT$ for silicon holey structure is 0.4, our sample represents a regime where electrical conductivity is preserved and thermal conductivity is only modestly reduced. Further reduction in thermal conductivity will likely result an inferior electrical conductivity [12].

Thermal conductivity measurements on silicon inverse opals show effective thermal conductivities $\lesssim 1$ W/mK and material thermal conductivities $\lesssim 10$ W/mK at room temperature. The relatively low thermal conductivities are significant in photonic applications where even relatively small absorption can cause significant temperature rise. In exploring phonon transport in these structures, we find that frequency-dependent, coherent phonon grain boundary scattering explains the data across the temperature range of the measurement down to 30 K. Compared to previous measurements, inverse opals provide access to more uniform grains across the entire sample since grain growth is restricted by the thickness of the silicon shell. On the basis of the thermal conductivity analysis, we hypothesize that the intergrain
region is thinner and possesses lesser disorder than typical polysilicon films. This is likely the reason for the clear frequency dependence in our data at low temperatures that is not observed in previous measurements. Assuming that inverse opals can be heavily doped similar to bulk polysilicon, these materials become interesting for thermoelectric energy conversion at high temperatures. Theoretical calculations [31] show $ZT \sim 0.6$ at 600 K, providing impetus for future experiments. This work provides thermal conductivity data useful in technological applications of inverse opals and insight into the physics of phonon heat conduction in these structures.

Future work could focus on lowering the limiting dimension before electrical conductivity is affected. This objective requires careful structure engineering and device integration. The target dimension is 50 nm [80]. However, it is unlikely to achieve significant enhancement in $ZT$ using silicon nanostructure. Beyond thermoelectric applications, selectively launching phonons with specific frequency could potentially decouple energy transport and phonon-electron interaction. Measurement wise, it could lead to the restoration of phonon drag in silicon nanostructures.
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