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Los Angeles

Thermal Transport in Nanoporous Materials for Energy Applications

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy in Mechanical Engineering

by

Jin Fang

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ABSTRACT OF THE DISSERTATION

Thermal Transport in Nanoporous Materials for Energy Applications

by

Jin Fang

Doctor of Philosophy in Mechanical Engineering University of California, Los Angeles, 2012 Professor Laurent G. Pilon, Chair

The present study investigates the complex relationship between nanostructures and microscale thermal transport in nanoporous thin films for energy applications. It experimentally and numerically demonstrates that the effective thermal conductivity of nanoporous materials can be tuned by controlling their nanoscale architectures including porosity, pore diameter, wall thickness, nanocrystal size, and crystallinity as well as surface passivation.

This study reports measurements of the cross-plane thermal conductivity of nanoporous thin films with various architectures between 25 and 315 K. Physics-based models combining phonon transport theory and effective medium approximations were developed to interpret the experimental data. Ordered mesoporous titania and silicon thin films were prepared based on evaporation-induced self-assembly method. Pure silica zeolite films were produced by either *in-situ* growth or by spin coating a zeolite nanoparticle suspension followed by crystal growth upon heating. These synthesized thin films were systematically and fully characterized. They featured ordered nanopores with porosity, pore diameter, and film thickness ranging from 30% to 59%, 0.5 to 25 nm, and 120 to 370 nm, respectively. Their dense matrix was amorphous, polycrystalline, or consisted of an aggregate of nanocrystals. The thermal conductivity of all synthesized nanoporous films increased monotonically with temperature within the temperature range considered. At low temperatures, the nanoporous films behaved like amorphous or strongly disordered materials and their thermal conductivity was proportional to T^n with n varied between 1 and 2.3. At high temperatures, the thermal conductivity increased slowly with temperature or reached a plateau due to strong phonon Umklapp scattering and the saturation of phonon modes. The presence of pores in *amorphous* mesoporous thin films had a purely geometrical effect by reducing the cross-sectional area through which heat can diffuse. By contrast, in *crystalline* mesoporous thin films the presence of pores also increased phonon scattering. In addition, the film thickness generally did not affect the measured thermal conductivity. Indeed, phonon scattering by pores and by nanocrystal grain boundary dominated over boundary scattering and were identified as the dominant scattering mechanisms for nanoscale energy transport in the synthesized nanoporous films.

This study further establishes that the effective thermal conductivity k_{eff} of crystalline nanoporous silicon was strongly affected not only by the porosity f_v and the systems length L_z but also by the pore interfacial area concentration A_i . A modified effective medium approximation combining kinetic theory and the coherent potential approximation suggested that k_{eff} was proportional to $(1-1.5f_v)$ and inversely proportional to the sum $(A_i/4+1/L_z)$. This scaling law was in excellent agreement with the thermal conductivity of nanoporous silicon predicted by molecular dynamics simulations for spherical pores as well as for cylindrical pores and vacancy defects.

Finally, this study demonstrated, using equilibrium molecular dynamics simulations, that surface passivation added another parameter for reducing the thermal conductivity of nanostructured materials. To do so, there should be strong acoustic vibrational modes coupling between surface and passivation atoms. For example, oxygen passivation reduced the thermal conductivity of nanoporous crystalline silicon. In addition, the effect of passivation reduced with temperature because of increasing contribution of Umklapp scattering.

These results could help establish new strategies to control the thermal conductivity of nanoporous materials for a wide range of applications including thermoelectric devices, supercapacitors, dye-sensitized solar cells, and hydrogen storage devices. The dissertation of Jin Fang is approved.

Adrienne Lavine Chih-Ming Ho Bruce S. Dunn Laurent G. Pilon, Committee Chair

University of California, Los Angeles 2012

This thesis is dedicated to my parents and my wife.

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VITA

2002-2006	B.S. Thermal Engineering, Tsinghua University, Beijing, China
2006-2008	M.S. Thermal Engineering, Tsinghua University, Beijing, China
2008-2012	Graduate student, Mechanical and Aerospace Engineering, University of California-Los Angeles, Los Angeles, CA, USA.

CHAPTER 1

Introduction

This chapter presents the motivation and objectives of the present study and the scope of this PhD thesis. First, an overview of the various applications of nanoporous materials is provided. Special attention is paid to mesoporous titania, zeolite, and mesoporous silicon. The importance of understanding and controlling thermal transport in these nanostructures is illustrated for selected energy applications. Then, synthesis of highly-ordered mesoporous thin films with tunable nanostructures is introduced. Finally, this chapter describes the objectives of the present research and concludes with the organization of the document.

1.1 Motivation of the Present Study

Nanoporous materials can be classified into three groups namely, micro-, meso-, and macroporous materials depending on their pore sizes [21]. Microporous material consists of pores with diameters up to 2 nm. The pores of mesoporous materials range from 2 to 50 nm in diameter while they are larger than 50 nm in macroporous materials [21].

Nanoporous materials have found numerous energy applications such as dye-sensitized solar cells, thermoelectric energy converters, supercapacitors, and hydrogen storage devices, to name a few. Indeed, introducing nanometer-size pores into thin films can enable the tuning of thermal, electrical, optical, and mechanical properties for the desired application. Understanding the complex relationship between nanostructures and properties in nanoporous materials is essential for material synthesis and for device design and optimization.

The following sections aim to introduce several applications of mesoporous titania, silicon as well as zeolite thin films. These are followed by a discussion of highly-ordered mesoporous thin films having nanostructure with a wide range of porosity, pore size, pore arrangement, and crystallinity.

1.1.1 Mesoporous Titania

Mesoporous titania (TiO₂) thin films have been considered for energy storage applications such as accumulators and electrochemical capacitors for their large surface area and redox reaction with lithium ions (Li⁺) in an organic electrolyte [22,23]. They have also been used as electrodes in dye-sensitized solar cells [24, 25] and as high proton conductivity porous exchange membranes in solid oxide fuel cells [26]. Moreover, Choi *et al.* [27] identified mesoporous TiO₂ thin films as promising thermal insulating materials for infrared sensors. Other applications include (i) highly specific chemical sensors and membranes [28], (ii) photocatalyst for water and air purification [29, 30], and (iii) optical coatings, emissive displays, and optoelectronics [31]. The following sections expands on dye-sensitized solar cells and electrochemical capacitors to illustrate the importance of understanding thermal transport in mesoporous titania thin films.

Electrochemical Capacitors

Figure 1.1 shows the power density versus energy density for various energy storage devices [1]. An ideal energy storage device should feature both large power and energy densities. However, batteries and fuel cells usually have large energy density but relatively small power density while conventional capacitors have high power density but low energy density. Electrochemical capacitors bridges the gap between batteries and conventional capacitors and have the potential to reach both high energy and power densities.

Alternatively, electrochemical capacitors, also termed supercapacitors [1], are attractive energy storage devices due to their (i) short charging time, (ii) large power density, and (iii) long cycle life time [23]. Figure 1.2 illustrates the two types of electrochemical capacitors, namely, electric double layer capacitors (EDLCs) and pseudocapacitors. In EDLCs, electric energy is stored physically through charge accumulation at the electrolyte/electrode interface. The amount of energy stored mainly depends on the surface area of the electrodes.



Figure 1.1: Power density versus energy density for various energy storage systems [1].

In pseudocapacitors, on the other hand, energy is stored not only in the form of physical charge in the electric double layer, but also in the fast and reversible surface redox processes between Lithium ions and transition metal oxide according to [32–35],

$$x\mathrm{Li}^{+} + \mathrm{M}_{n}\mathrm{O}_{p} + x\mathrm{e}^{-} \rightleftharpoons \mathrm{Li}_{x}\mathrm{M}_{n}\mathrm{O}_{p} \tag{1.1}$$

Here, M_nO_p can be chosen from a variety of transition metal oxides such as RuO₂, TiO₂, MnO₂, V₂O₅, and Nb₂O₅ [35].

Block copolymer templated ordered mesoporous TiO_2 thin film electrodes were reported to have large pseudocapacitance in propylene carbonate solution of LiClO_4 [22, 23] thanks to their large surface area concentration as well as the surface redox reactions. Detailed discussion of the mesoporous TiO_2 electrochemical capacitors can be found in Refs. [22, 23]

During charging and discharging, electrochemical capacitors lose energy in the form of Joule heating within the capacitor cells [36]. The heat generation rate depends on the design of the electrochemical capacitors and on the charging/discharging dynamics [36]. Potential temperature rise and difference between the cells will cause voltage imbalance in cells con-



Figure 1.2: Illustration of the two types of electrochemical capacitors, including electric double layer capacitors (EDLCs) and pseudocapacitors, and the associated charge storage mechanisms.

nected in a series resulting in shorter cell lifetime [36–41]. In addition, high temperature may also result in increased self-discharge rates [37, 39–41] and possibly electrolyte evaporation, which can damage the cell [37]. Therefore, thermal management systems are required to operate electrochemical capacitors under uniform and appropriate temperature. Here also, knowing the thermal properties of mesoporous TiO_2 is essential for the design, optimization, and operation of electrochemical capacitors.

Dye-Sensitized Solar Cells

Dye-sensitized solar cells (DSSCs) are drawing worldwide attention because of their high efficiency and low manufacturing cost [24, 25]. Figure 1.3 shows a schematic and functioning principle of a typical dye-sensitized solar cell [2]. It is composed of mesoporous TiO_2 sandwiched between transparent conductive electrodes and filled with a dye sensitizer. The ensemble is impregnated with an electrolyte solution typically an organic solution of iodide I_3^-/I^- redox system [42]. Under sunlight irradiation, the dye molecules become photo-excited and inject electrons into the conduction band of the mesoporous TiO₂. They are regenerated by the redox system in the organic electrolyte. The redox system itself is regenerated at the counter electrode by electrons that have passed through the outside load [43].



Figure 1.3: Schematic and functioning principle of a dye-sensitized solar cell [2].

Grätzel [42] indicated that the performance of a DSSC was insensitive to its internal temperature change. He concluded that raising the temperature from 20 to 60°C had no effect on the power conversion efficiency [42]. However, the temperature stability of the liquid electrolyte remains a concern [44]. Indeed, at low temperatures the electrolyte can freeze, disrupting power production and leading to physical damage to the cell [44]. High temperatures induce high vapor pressure of the organic solvent, which may compromise sealing of the device [44]. Solid state electrolytes were developed to avoid the above problems [42]. However, the open circuit voltage was found to decrease linearly with increasing temperature from 25 to 80°C [45]. Therefore, understanding the thermal behavior of DSSCs' various components, and in particular that of the mesoporous TiO₂ electrodes, is of great importance to ensure high efficiency and long life time.

1.1.2 Zeolite

Zeolites are a group of nanoporous crystalline aluminosilicates with uniform micropores. They differ by their crystalline structure, microporosity, and their framework density defined as the number of tetrahedrally coordinated atoms per 1000 Å³. For example, Figures 1.4(a) and 1.4(b) show the microporous frameworks of MFI (Socony Mobile-five) and MEL (Socony Mobile-eleven) zeolite, respectively [3]. The MFI structure has 0.55 nm wide sinusoidal channels along the *a*-axis and 0.53 nm wide straight channels along the *b*-axis [46]. The MEL structure has 0.54 nm wide straight channels along both the *a*- and *b*-axis [46]. The presence of these micropores contributes to the so-called microporosity. The framework density of PSZ MEL and MFI is 17.4 and 18.4, respectively [46]. Pure silica zeolites (PSZs) have no aluminum in their framework.



Figure 1.4: Schematics of the microporous framework of (a) MFI (Socony Mobile-five) and (b) MEL (Socony Mobile-eleven) zeolite [3].

Zeolites have been considered as adsorbents for sorption-based heat exchangers for heat recovery and cooling applications [47–50]. They are also of interest for hydrogen storage as molecular sieves and as low-dielectric constant materials for very large scale integrated circuits [46,51]. In addition, there is an emerging trend to use zeolite thin films in various micro/nanoscale applications, such as filters for air pollutants, microreactors, and miniature gas sensors [21,52–55]. In all these applications, knowledge of thermal properties of zeolites over a wide range of temperature is of significant importance for their practical implementation in devices and systems.

1.1.3 Porous Silicon

Porous silicon has been the subject of intense studies due to its wide range of applications. For example, porous silicon has been used in optoelectronics for its photoluminescence properties [56]. Optoelectronic devices generate heat by either Joule heating or photon absorption. Thus, knowing the thermal conductivity of porous silicon is important for proper thermal management of these devices [57]. In addition, porous silicon has been used as thermal insulator and sensor in microsystem technology thanks to its low thermal conductivity and rigid solid structure [58]. More recently, nanoporous silicon was also found promising in high energetic MEMS devices [59–65]. The presence of nanosize pores creates very large internal surface area. Combining with oxygen source and heat input, strong exothermic reactions take place within the nanoporous silicon which could be used for microthrusters, microinitiators, and gas generation for actuators [64]. Here also, the thermal conductivity of nanoporous silicon is essential to the design and operation of these MEMS devices.

Moreover, porous silicon is a potentially efficient thermoelectric material for energy harvesting applications with an operating temperature typical ranging from 573 to 1273 K [19, 66, 67]. Thermoelectric materials utilize the Seebeck effect to convert a temperature gradient directly into electricity. Their performance is described by the figure of merit ZTgiven by $ZT = \sigma TS^2/k$, where T is absolute temperature while σ and k are the electrical and thermal conductivities, respectively. The Seebeck coefficient S depends on the temperature and on the material [68]. Good thermoelectric materials feature high electrical conductivity and high Seebeck coefficient but low thermal conductivity. However, it is difficult to find such materials due to the interdependence among σ , S, and k [68]. As a thermoelectric material, bulk dense crystalline Si is considered inefficient with ZT around 0.003 at room temperature [66]. However, according to recent simulations, well-ordered nanoporous silicon with pore diameter between 0.6 and 1.2 nm and porosity between 12% and 30% may feature ZT of about 1.0 at 300 K [66]. This significant increase in ZT was attributed to the large reduction in k accompanied by only moderate changes in σ and S [19, 66]. Practically, a ZT value of about 3.0 could lead to efficient solid state energy conversion [68]. Thus, the thermal conductivity of nanoporous silicon needs to be tuned in order to further improve its figure of merit. It is therefore, important to first understand and predict thermal transport in nanoporous crystalline silicon.

1.1.4 Highly-Ordered Mesoporous Materials

As already discussed, understanding and controlling thermal transport properties of nanoporous materials are of significant importance to the device design and optimization. The present study pays special attention to highly-ordered mesoporous titania and silicon thin films with tunable nanostructures. The highly-ordered mesoporous titania thin films were synthesized by calcination of polymer/titania composites produced by evaporation-induced selfassembly (EISA) using titania precursors and block copolymer templates. The ordered mesoporous silicon thin films were produced by EISA of ordered mesoporous silica (SiO₂) followed by magnesium reduction to remove oxygen. Descriptions of the synthetic methods are presented in more detail in Chapters 3 and 5. Figures 1.5(a) and 1.5(b) show SEM micrographs of KLE [poly(ethylene-co-butylene)-block-poly(ethylene oxide)] templated highlyordered amorphous and crystalline mesoporous titania thin films investigated in the present study, respectively. They illustrate the highly-ordered mesoporous structure of the films.

These ordered mesoporous thin films are interesting because their nanoscale morphology, such as porosity, pore size, pore arrangement, wall thickness, and crystallinity, can be tuned over a fairly broad range using different copolymer templates and different concentrations as well as different synthesis temperatures [69]. Therefore, this synthesis method offers the ability to control the thermal conductivity of mesoporous thin films by tuning their nanoscale morphology.



Figure 1.5: SEM micrographs of KLE [poly(ethylene-co-butylene)-block-poly(ethylene oxide)] templated highly-ordered (a) amorphous and (b) crystalline mesoporous TiO₂ thin films.

1.2 Objectives of the Present Study

The present study focuses on the microscale thermal transport in ordered mesoporous titania and silicon as well as pure silica zeolite thin films. The study is unique in that it aims not only to investigate thermal conductivity of nanoporous thin films with tunable structures but also to gain more insight into the complex relationship between nanostructures and properties of these novel materials. This will be useful in designing nanostructured materials with desired thermal conductivity for various applications. Specific objectives of the present study can be divided into two major parts:

1.2.1 Experimental Study of Nanoporous Thin Film Thermal Conductivity

Accurate measurements of the thermal conductivity of nanoporous materials over a wide range of temperature is valuable for both theoretical and numerical study, as well as for various engineering applications. Experimentally, the present study aims to achieve the following objectives:

1. To build an accurate experimental apparatus using the 3ω method to measure nanoporous

thin film thermal conductivity between 25 and 315 K. Validation of the apparatus will be performed by measuring the thermal conductivity of high purity single crystal silicon and thermally grown amorphous silicon dioxide films.

- 2. To synthesize and characterize dense and highly ordered mesoporous titania thin films, MEL and MFI pure silica zeolite thin films, and ordered mesoporous nanocrystalline silicon thin films with various porosity, crystallinity, pore size, and shape. Characterization should provide detailed morphological information of the thin films.
- 3. To systematically investigate various effects on the effective cross-plane thermal conductivity of ordered mesoporous titania, pure silica zeolite, and ordered mesoporous nanocrystalline silicon thin films between 25 and 315 K. Parameters of interest include temperature, film thickness, porosity, pore diameter, nanocrystal size, wall thickness, and crystallinity.
- 4. To identify the key structural parameters that strongly affect the thermal conductivity.

1.2.2 Modeling for the Nanoporous Thin Films

In the modeling aspect, the present study intends to achieve the following objectives:

- 1. To develop physics-based theoretical models combining effective medium approximations and phonon transport theory to predict the thermal conductivity of nanoporous thin films. The theoretical models should be able to capture the temperature dependence of thermal conductivity of ordered mesoporous titania, pure silica zeolite, and ordered mesoporous silicon thin films.
- 2. To identify the dominant phonon scattering mechanisms in nanoporous thin films with respects to the nanoscale architecture. Scattering mechanisms include phonon scattering by the film boundaries, the pores, the nanocrystal grain boundaries, as well as phonon Umklapp scattering, and scattering on the surface passivation layer. The result will enable one to better interpret the experimental data and to design novel nanostructured materials with the desired thermal conductivity for various applications.

- 3. To develop a physics-based model predicting the effects of porosity, pore diameter, and system length on the thermal conductivity of nanoporous crystalline silicon. This will be achieved by using kinetic theory, effective medium approximation, and nonequilibrium molecular dynamics method.
- 4. To derive scaling laws relating the thermal conductivity to key structural parameters such as porosity, interfacial area concentration, and system length.
- 5. To investigate the effect of surface passivation on the thermal conductivity of nanoporous crystalline silicon and its underlying physics. Particular attention will be paid to hydrogen and oxygen surface passivation. The result will be used to examine the feasibility of tuning thermal conductivity of nanoporous silicon thanks to surface passivation.

1.3 Organization of the Document

First, a general background of thin film thermal conductivity measurement and thermal transport physics is presented in Chapter 2. Chapters 3, 4, and 5 present experimental results and physical modeling of the thermal conductivity of (i) ordered mesoporous titania thin films, (ii) pure silica zeolite thin films, and (iii) ordered mesoporous nanocrystalline silicon thin films, respectively. Each chapter systematically describes the synthesis method, the detailed structural characterization, and the physical modeling and comparison with experimental results for each nanoporous material considered. Chapter 6 presents molecular dynamics study and scaling analysis for the thermal conductivity of nanoporous crystalline silicon. The feasibility of tuning thermal conductivity of nanoporous silicon by surface passivation is discussed in Chapter 7. Finally, Chapter 8 summarizes the main findings of the present research and provides recommendations for future work.

Nomenclature

k	Thermal conductivity $[{\rm W}/{\rm m}{\cdot}{\rm K}]$
S	Seebeck coefficient $[V/K]$
Т	Temperature [K]
ZT	Thermoelectric figure of merit [-]

Greek Symbols

σ	Electrical	conductivity	[S]	/ml
0	Liccurat	conductivity	[127	111

CHAPTER 2

Background

The present chapter aims to provide the reader with a general background about experimental techniques as well as physical phenomena and associated modeling methods used to investigate microscale thermal transport. It supports the analysis and discussions presented in the subsequent chapters.

2.1 Thin Film Thermal Conductivity Measurements

The discussion here does not intend to present a comprehensive review of various experimental methods. More information on various experimental techniques can be found in Refs. [4,70]

2.1.1 Overview

Techniques for thin film thermal conductivity measurement can be categorized into (i) optical heating and sensing methods and (ii) electrical heating and sensing methods [70]. The general idea of the optical heating and sensing methods is to impose a sudden or periodic high radiation flux to heat the sample of interest. Then, the evolution of temperature decay at the sample surface is recorded by measuring temperature dependent material properties using a probe laser. The temperature temporal evolution depends on the thermal diffusivity α of the sample [71]. Then, its thermal conductivity k can be derived from the relation of $k = \alpha/\rho c_p$, where ρc_p is the volumetric heat capacity of the sample. Note that the volumetric specific heat is often unavailable for nanoporous thin films and therefore requires independent measurement. The optical heating and sensing methods are indirect measurement methods of thermal conductivity. Finally, there are various configurations of the optical heating and sensing methods, depending on how the surface temperature is measured [70]. For example, the thermoreflectance method measures the temperature dependent reflectance to retrieve the surface temperature [72]. The Mirage method [73,74] and the photothermal displacement method [75] are based on laser deflection caused by the temperature dependent refractive index change and the thermal expansion of the sample, respectively.

On the other hand, electrical heating and sensing methods use microheaters and sensors patterned on sample films to heat up dielectric or semiconductor samples and measure the corresponding temperature rise, respectively. Thermal conductivity can then be retrieved from temperature changes in the sample caused by Joule heating [4,70]. The advantages of such methods lie in the facts that (i) the heating power and the resulting sample temperature rise can be accurately controlled and measured and (ii) the thermal conductivity can be measured directly [4,70]. The 3ω method [9] is one of the most wide used electrical heating and sensing methods. It has been extensively used to measure thermal conductivity of dielectric and semiconductor thin films [4,9,76].

2.1.2 The 3ω Method

The 3ω method measures surface temperature oscillation, in conjunction with an approximate analytical solution, to determine thermal conductivity of bulk as well as thin film materials [9,76,77]. Figure 2.1 shows a schematic of a typical test section structure using the 3ω method. A metallic wire of width 2b and length L, serving as both a line heater and a thermometer, is patterned on top of a thin film of interest. An AC current at frequency ω is driven through the wire and heats the sample up, resulting in a surface temperature oscillation at frequency 2ω . It will then cause the fluctuation in electrical resistance of the metallic wire. As a result, this process produces a measurable signal at a frequency which is three times the driving frequency ω . Thermal conductivity of the thin film can then be retrieved by analyzing the third harmonic voltage drop $V_{3\omega}$ across the metallic wire. [9,76,77].

The temperature oscillation amplitude in both the sample film and its substrate ΔT_{f+sub}



Figure 2.1: Schematic of a thin film test section using the 3ω method.

can be expressed as [77],

$$\Delta T_{f+sub} = \frac{2V_{3\omega}}{\gamma V_{\omega}} \tag{2.1}$$

where $\gamma = (dR_e/dT)/R_e$ is the temperature coefficient of resistance of the metallic wire and R_e is its electrical resistance. Similarly, the substrate temperature oscillation amplitude ΔT_{sub} can be determined when the metallic wire is patterned on the substrate directly. Finally, the thermal conductivity of the film of interest is expressed as [76, 77],

$$k = \frac{Pt_f}{2bL\left(\Delta T_{f+sub} - \Delta T_{sub}\right)},\tag{2.2}$$

where ΔT_{f+sub} and ΔT_{f+sub} should correspond to the same power dissipation P in the metallic wire.

2.2 Thermal Transport Physics

This section presents several important concepts and models used to describe and predict microscale thermal transport. They will be used to interpret experimental data and determine relationship between nanostructures and properties throughout the study.

2.2.1 Theoretical Background

Phonon

Phonons are quantized lattice vibrations and are major energy carriers in crystalline solids. Phonons are bosons and like photons they can be treated as waves or as particles. When the lattice vibration direction is perpendicular to the energy propagation direction, the phonons are said to be transversely polarized. When the vibrations are along the direction of energy propagation, the phonons are longitudinally polarized.

The phonon wavevector \vec{K} represents the momentum of a phonon and has the same direction as the wave propagation. The norm of the wavevector is expressed as its wavenumber as,

$$K = \frac{2\pi}{\lambda} = \frac{2\pi v_g}{\omega},\tag{2.3}$$

where v_g and ω are the phonon group velocity or wave propagation speed and phonon angular frequency in rad/s, respectively.

The momentum of a phonon can be related to its wavevector \vec{K} by [78],

$$\vec{p} = \hbar \vec{K}.\tag{2.4}$$

Here, $\hbar = h/2\pi = 1.05457148 \times 10^{-34} \text{ m}^2 \cdot \text{kg/s}$ is the reduced Planck's constant. The total energy E_n could exist only in discrete quanta so that [4,78],

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega,\tag{2.5}$$

where n is an integer representing the number of phonons and $E_0 = \hbar \omega/2$ is called the zero-point energy.

Bose-Einstein Distribution

The probability that a phonon will have energy $E = \hbar \omega$ at equilibrium temperature T is the so-called energy distribution function. For phonons, this probability is described by the Bose-Einstein statistics expressed as [78],
$$f_{BE}(\omega,T) = \frac{1}{e^{\hbar\omega/k_BT} - 1} \tag{2.6}$$

Here, k_B is the Boltzmann constant equal to 1.380×10^{-23} J/K. In the limiting cases, $f_{BE}(\omega, T)$ goes to infinity as E tends to zero and vanishes for energy E much larger than k_BT .

Dispersion Relation

The relationship between phonon frequency ω and wavevector \vec{K} is called the dispersion relation and may be different along different wavevector directions. Figure 2.2 shows a typical dispersion relation for a crystalline solid [4]. It indicates that phonons can follow an acoustic and an optical branch. Each branch can support longitudinal as well as transverse polarizations. The acoustic branch represents the lattice vibration at relative low frequencies. It strongly influences heat conduction in a crystal solid. One the other hand, the optical branch corresponds to higher frequencies. Indeed, it is so named because it mainly affects optical properties of a crystal solid [4]. The first Brillouin zone, is such that $-\pi/a \leq K \leq \pi/a$ where a is the lattice constant. It corresponds to the K-space of a crystal lattice with an atomic spacing of a. The allowable wavevector in a crystal solid is confined to the first Brillouin zone [78].

Group Velocity

The speed at which energy carried by phonons propagates is the so-called group velocity, which is also the speed of sound in crystal lattice. It is defined as $v_{g,i} = d\omega_i/dK$ for the i^{th} polarization. Figure 2.2 shows that, in the long wavelength limit as $K \to 0$, a linear ω -K relation forms in the acoustic branch, indicating that the group velocity or the speed of sound is independent of frequency. On the other hand, the optical phonon group velocity is negligible compared with that of the acoustic phonon. Therefore, optical phonons are typically assumed not to contribute to heat conduction [4].



Figure 2.2: Dispersion relation for crystal vibrations [4].

Density of States

The phonon density of states is defined as the number of phonon modes per unit volume of material between wavevector K and K + dK. Figure 2.3 shows a reciprocal lattice in the wavevector space (K-space) of a crystalline solid of size $L \times L \times L$ where each point represents one phonon mode. In the K-space, the volume of a sphere of radius K is equal to $4\pi K^3/3$. One can show that every phonon modes occupies a cube of volume $(2\pi/L)^3$ [78]. Thus, the number of phonon modes in a sphere of radius K in the wavevector space is expressed as [4,78],

$$N = \frac{4\pi K^3/3}{(2\pi/L)^3}.$$
(2.7)

The number of modes per unit volume can then be defined as [4, 78],

$$\frac{N}{V} = \frac{N}{L^3} = \frac{K^3}{6\pi^2}.$$
(2.8)

Finally, the phonon density of states is expressed as [4, 78],

$$\mathcal{D}(K) = \frac{\mathrm{d}(N/V)}{\mathrm{d}K} = \frac{K^2}{2\pi^2}.$$
(2.9)

In the three-dimensional K-space shown in Figure 2.3, the phonon density of states is equivalent to the number of modes enclosed by a thin spherical shell of inner radius K and thickness



Figure 2.3: A reciprocal lattice in the wavevector space of a crystalline solid [4].

Specific Heat

The thermal energy per unit volume of material u as a function of wavenumber K is given by [4,78],

$$u = \sum_{i=1}^{3} \int_{K} \hbar \omega_i(K) \mathcal{D}_i(K) f_{BE,i}(K) \mathrm{d}K, \qquad (2.10)$$

where the summation is over all three polarizations. Based on thermodynamics, the specific heat c_v can then be found by differentiating Equation (2.10) with respect to temperature as [4,78],

$$c_v = \left(\frac{\mathrm{d}u}{\mathrm{d}T}\right)_v = \sum_{i=1}^3 \int_K \hbar\omega_i(K) \mathcal{D}_i(K) \frac{\partial f_{BE,i}(K)}{\partial T} \mathrm{d}K.$$
 (2.11)

The Debye Model

The Debye model assumes the following,

1. The group velocity $v_{g,i}$ of phonons with polarization *i* is constant so that $\omega_i = v_{g,i}K$.

 $\mathrm{d}K.$

Physically, acoustic phonons dominate energy transport and travel at the speed of sound [79]. This approximation is valid at low frequency region where acoustic phonons populate but is not appropriate at high frequency.

2. The phonon frequency cannot be larger than the Debye cut-off frequency $\omega_{D,i}$ for polarization *i* defined as [78],

$$\omega_{D,i} = v_{g,i} K_{D,i}, \tag{2.12}$$

where $K_{D,i}$ represents the Debye cut-off wavenumber for polarization *i*. In the Debye model, phonon wavevector are not allowed to be larger than $K_{D,i}$. Physically, this corresponds to the fact that phonons cannot assume wavelength smaller than twice the atomic spacing. Figure 2.2 illustrates the dispersion relation given by the Debye model and Equation (2.12).

3. The Debye density of state $\mathcal{D}_{D,i}$ as a function of frequency ω_i for phonons with polarization *i* is given by,

$$\mathcal{D}_{D,i}(\omega_i) = \frac{K^2}{2\pi^2} = \frac{3}{2\pi^2} \frac{\omega_i^2}{v_{g,i}^3} \quad \text{with} \quad 0 \le \omega_i \le \omega_{D,i}.$$
(2.13)

Phonon Scattering

As discussed already, phonons are dominant energy carriers in semiconductors and dielectric materials. Resistance to heat transfer in a porous material is determined by phonon scattering with (i) electrons, (ii) impurities/defects, (iii) boundaries, and (iv) other phonons, especially Umklapp scattering. Figure 2.4 shows various phonon scattering events taking place in a porous thin film. Phonon relaxation time represents the length of time it takes for a phonon to relax back to an equilibrium state after a certain scattering event [4]. Different types of phonon scattering can be described by their associated relaxation time.

Phonon-electron scattering can affect energy transport for doped materials. It becomes important at high temperature where electrons contribute to energy transport. It can be neglected in the present study.

In real crystals, there are defects such as impurities, dopants and dislocations. Phonons



Figure 2.4: Phonon scattering in a porous thin film.

can be scattered by these defects. The relaxation time for phonon-defect scattering τ_D can be expressed by the Rayleigh law as [4],

$$\tau_D^{-1} = A\omega^4 \tag{2.14}$$

where A is an empirical parameter and ω is the phonon frequency.

Phonons can also scatter with various boundaries such as film boundary, pore boundary, and crystal grain boundary. The boundary scattering relaxation time τ_B is typically expressed as [4],

$$\tau_B^{-1} = v_g / E, \tag{2.15}$$

where v_g is the phonon group velocity and E is a characteristic length which is often fitted to experimental data. In nanoporous thin films, main parameters that affect E are film thickness, crystal grain size, and wall thickness between two adjacent pores.

Equation (2.15) is based on the assumption that phonon-boundary scattering is frequency independent or "gray". A more cautious approach would treat τ_B as frequency dependent [15]. The detailed boundary conditions, such as material compositions, roughness, and surface passivation, could also affects phonon scattering. For example, phonon leakage, i.e., the transmission of lattice vibrational energy across the boundary, can happen when phonons scatter at a boundary where two dissimilar materials meet [80,80–82]. In nanoporous materials, no phonon leakage will be expected since the pores are empty. In addition, recent molecular dynamics study shows that the surface passivation at boundaries may also affect phonon scattering. For example, hydrogen passivation on the edges of graphene nanoribbons reduced their thermal conductivity by about 40-60% between 100 and 300 K [83,84]. This was attributed to increased phonon scattering by the hydrogen passivated boundaries [83,84].

There are two types of phonon-phonon scattering, namely, Umklapp and normal scattering. Figure 2.5 illustrates phonon-phonon scattering where (a) two phonons interact to produce a third phonon, (b) one phonon is converted into two phonons upon the scattering events, or (c) two phonons interact to produce a third phonon with a reciprocal lattice vector [85]. For these scattering events, the momentum conservation equation can be written as [78],

$$\vec{K}_1 + \vec{K}_2 - \vec{K}_3 = \vec{G} \tag{2.16}$$

where \vec{K}_1, \vec{K}_2 , and \vec{K}_3 are phonon wavevectors and \vec{G} is a reciprocal lattice vector. The only meaningful wavevector \vec{K} lies in the first Brillouin zone. Thus, any wavevector produced in a scattering beyond the first Brillouin zone must be brought back into it by addition of \vec{G} . Phonon normal scattering takes place when $\vec{G} = \vec{0}$ and it does not affect energy transport [Figures 2.5(a) and 2.5(b)]. When $\vec{G} \neq \vec{0}$ as shown in Figure 2.5(c), phonon Umklapp scattering occurs which strongly affect energy transport. A commonly used relaxation time model for Umklapp scattering is expressed as [4],

$$\tau_U^{-1} = BT\omega^2 \exp(-C/T),$$
 (2.17)

where B and C are empirical parameters which can be obtained by data fitting.

Finally, assuming that the different phonon scattering events are independent, the total effective phonon relaxation time τ_{eff} can be expressed using the Matthiessen rule [86],

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_U} + \frac{1}{\tau_B} + \frac{1}{\tau_D}$$
(2.18)

More information on phonon scattering and various relaxation time models can be found in Refs. [4, 17, 86, 87]



Figure 2.5: Different types of phonon-phonon scattering, namely (a) two phonons interact to produce a third phonon, (b) one phonon is converted into two phonons, and (c) two phonons interact to produce a third phonon with a reciprocal lattice vector.

2.2.2 Physical Modeling of Thermal Conductivity

Kinetic Theory Model

From kinetic theory, the net heat flux q''_z in the z-direction in a solid can be expressed as [4,78],

$$q_z'' = -\frac{1}{3}c_v v_g l \frac{\mathrm{d}T}{\mathrm{d}z} \tag{2.19}$$

where c_v is the specific heat in J/kg·K, l is the average phonon mean free path corresponding to the average distance traveled by a phonon between two successive scattering events, and dT/dz is the temperature gradient in the z-direction.

By comparing with Fourier's law given by $q''_z = -k(dT/dz)$, the thermal conductivity k_z can be expressed as [4,78],

$$k_z = \frac{1}{3}c_v v_g l. \tag{2.20}$$

Cahill-Pohl Thermal Conductivity Model

Einstein [88] proposed a model for heat conduction in amorphous solids. He assumed that (i) all atoms vibrated as harmonic oscillators at the same frequency and (ii) the phase of neighboring oscillators were uncorrelated [4]. Cahill and Pohl [4] improved this model by considering the coherence of a crystal wave over a distance on the order of a mean free path. The Cahill-Pohl model divided a solid into localized regions of size $\lambda/2$, where λ is the wavelength of a given phonon mode. It also assumed that these localized regions vibrate at frequencies equal to $\omega = 2\pi v_g/\lambda$, where v_g is the speed of sound [89,90]. Based on these assumptions, the thermal conductivity of a strongly disordered material k_{CP} as a function of temperature is expressed as [89],

$$k_{CP}(T) = \left(\frac{\pi}{6}\right)^{1/3} k_B n^{2/3} \sum_{i=1}^{3} v_{g,i} \left(\frac{T}{\theta_i}\right)^2 \int_0^{\theta_i/T} \frac{x^3 e^x}{\left(e^x - 1\right)^2} \mathrm{d}x.$$
 (2.21)

where $k_B = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant, n is the number of atoms per unit volume of material. The summation is performed over three polarizations including two transverse (i = 1, 2) and one longitudinal (i = 3) polarizations with the associated speed of sound $v_{g,i}$ and characteristic temperature $\theta_i = v_{g,i}(\hbar/k_B) \times (6\pi^2 n)^{1/3}$. This model has been termed the minimum thermal conductivity model. It has been applied for amorphous and strongly disordered polycrystalline materials [4].

Callaway Thermal Conductivity Model

Callaway model [86,87] is based on the following assumptions: (i) phonons are the only heat carriers, (ii) the Debye model is assumed to be valid, i.e., the phonons have a constant group velocity v_g and cannot have a frequency greater than the Debye cut-off frequency ω_D , (iii) all three phonon polarizations are treated identically, (iv) optical phonons do not contribute to heat conduction due to their small group velocities, (v) the phase of the phonons is not accounted for, thus neglecting interference effects; (vi) the scattering mechanisms are independent and the single model relaxation time approximation is used to estimate total relaxation time, (vii) thermal expansion is neglected, and (viii) the medium is isotropic [91]. Then, the Callaway thermal conductivity $k_{Callaway}$ of a bulk crystalline solid at temperature T can be expressed as [86,87],

$$k_{Callaway} = \frac{k_B}{2\pi^2 v_g} \left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\theta_D/T} \tau_{eff} \frac{x^4 e^x}{(e^x - 1)^2} \mathrm{d}x \tag{2.22}$$

where v_g is the phonon group velocity in the material, θ_D is the Debye temperature, and τ_{eff} is the effective phonon relaxation time.

Effective Medium Approximation

The physical models discussed above are for dense (non-porous) materials. For porous materials, the effect of porosity on various properties is usually accounted for by some effective medium approximations (EMAs). Numerous EMAs have been developed in order to predict the effective thermal conductivity k_{eff} of porous materials [69,92]. Here, the thermal conductivity of gas in the pores in nanoporous thin films, denoted by k_d , is negligibly small as predicted by kinetic theory for very large Knudsen number Kn according to [92,93],

$$k_d = \frac{k_{d,0}}{1 + 2\beta \text{Kn}} \quad \text{where} \quad \text{Kn} = \frac{\ell}{d_p} = \frac{k_B T}{\sqrt{2\pi\sigma^2 p d_p}}.$$
 (2.23)

Here, ℓ is the gas molecule mean free path inside the pores of diameter d_p , σ is the gas molecule diameter, p is the pressure, and r is the diameter of the gas molecules. The coefficient β is equal to 1.5 for air, and $k_{d,0}$ is the thermal conductivity of bulk air corresponding to Kn = 0.0 and equal to 0.026 W/m·K at atmospheric pressure and room temperature [93]. It is evident that for pores a few nanometer in diameter Kn becomes very large at atmospheric pressure and room temperature resulting in $k_d \approx 0.0$.

In the case of nanoporous materials where the pore thermal conductivity can be neglected, EMAs typically provide expressions for k_{eff} as the product of the dense matrix thermal conductivity k_m and a function of porosity $\Psi(f_v)$, i.e., $k_{eff} = k_m \Psi(f_v)$. For example, the series model is simply expressed as $\Psi(f_v) = 1 - f_v$. In addition, the Russell model [94] gives $\Psi_{Russell}(f_v) = (1 - f_v^{2/3})/(1 - f_v^{2/3} + f_v)$ while the Eucken model [95] uses $\Psi_{Eucken}(f_v) =$ $(1 - f_v)/(1 + f_v/2)$. These models were previously used to model the effective thermal conductivity of microporous silicon with periodically aligned cylindrical pores and porosity of 23% and 26% [96, 97].

Moreover, the coherent potential model is expressed as [8, 98],

$$k_{eff} = k_m \Psi_{cp}(f_v) = k_m (1 - 1.5 f_v).$$
(2.24)

This model was first derived by Landauer [98] for the effective dielectric properties of random mixtures of spherical inclusions in a continuous matrix. The main assumption was that "a region of type 1 is not preferentially surrounded by either other regions of type 1 or by regions

of type 2" [98]. Therefore, porous materials having very small or very large porosity do not satisfy this assumption. Cahill and Allen [8] successfully applied the coherent potential model to predict the thermal conductivity of Vycor glass from 30 to 300 K with pore diameter and porosity approximately equal to 10 nm and 30%, respectively. More recently, this model was also found to agree well with predictions of thermal conductivity of amorphous mesoporous silica at 300 K obtained by non-equilibrium MD simulations [92].

2.2.3 Molecular Dynamics Simulations

Molecular dynamics (MD) simulations represent an interesting alternative to both experiments and physical modeling previously discussed. They require very few assumptions aside from the interaction potential. They solve the Newton's equation of motion of individual atom whose interaction forces are governed by an empirical interatomic potential. For the i^{th} particle with a mass m_i , its trajectory $\vec{r}_i(t)$ is expressed as,

$$m_i \frac{\mathrm{d}^2 \vec{r_i}}{\mathrm{d}t^2} = \sum_{j=1, j \neq i}^N \vec{F_{ij}} \quad (i = 1, 2, ..., N) \quad \text{where} \quad \vec{F} = -\nabla U \tag{2.25}$$

where N is the total number of atoms, \vec{F}_{ij} denotes the force imposed on atom *i* from atom *j*, and U is the interaction potential. The summation is carried over all other atoms in the system. Figure 2.6 shows a schematic of a typical interatomic potential U as a function of interatomic distance *r*. The potential reaches a minimum when the molecules reach their equilibrium positions with a separation distance r_0 .

The two most commonly used MD simulation methods to predict thermal conductivity are the Green-Kubo method [16,99–102] and the Müller-Plathe method [16,99,103,104].

The Green-Kubo method is an equilibrium molecular dynamics (EMD) method. It consists of extracting the transport properties at equilibrium through the fluctuation-dissipation theorem using relations derived by Green and Kubo [101, 102]. Indeed, perturbations are induced by the fluctuations of the system's temperature, at equilibrium. The response of the system to these perturbations depends on its thermal conductivity. In an ensemble of constant number of atoms, volume and energy (NVE), the thermal conductivity can



Figure 2.6: Schematic of a typical interatomic potential.

thus be evaluated through the time integration of the heat current autocorrelation function (HCACF) [101, 102]. The thermal conductivity of the system is related to how long this heat current remains correlated with itself. In a material with a small thermal conductivity, the correlation will be short lived because fluctuations from equilibrium dissipate rapidly. However, the correlation will be long lasting in a material with a large thermal conductivity. Finally, dynamic properties such as vibrational density of states can be conveniently calculated from EMD simulations. However, very long simulation times are usually required to sufficiently converge the autocorrelation function.

The Müller-Plathe method or the "direct method" is a non-equilibrium molecular dynamics (NEMD) simulation method [16]. It predicts the thermal conductivity from the temperature gradient and heat flux flowing through a simulation system. The general idea of the Müller-Plathe method consists of imposing a constant heat flux q''_z to the system in the z-direction, resulting in a steady state temperature gradient dT/dz, just as in experimental measurements. The thermal conductivity k_z in the z-direction can then be calculated using Fourier's law $k_z = -q''_z/(dT/dz)$. This method does not need to calculate the slowly converged autocorrelation function as in EMD simulations. Therefore, it is computationally more efficient [16, 103]. However, it cannot provide information on the system's dynamic properties such as dispersion relation and vibrational density of states. It has already been implemented to predict the thermal conductivity of bulk dense materials [16, 105–108] as well as nanoparticles and nanowires [109].

2.3 Conclusions

The present chapter first provided an overview on the thin film thermal conductivity measurement techniques and in particular the 3ω method. It then presented a general background of thermal physics and of the associated modeling. Alternatively, molecular dynamics simulations can be used to predict the thermal conductivity of dense or nanoporous materials. Physical modeling and MD simulations will be performed, in conjunction with experimental study, to gain insight into the thermal transport phenomena in nanoporous thin films. Note that more detailed background and current state of knowledge related to specific materials will be introduced in the subsequent chapters.

Nomenclature

a	Lattice constant [m]
b	Half width of the metallic wire [m]
c_p	Specific heat for constant pressure $[{\rm J/kg{\cdot}K}]$
c_v	Specific heat for constant volume $[{\rm J/kg{\cdot}K}]$
E	Phonon energy [J]
f_{BE}	Bose-Einstein distribution
f_v	Porosity
$\vec{F}_{i,j}$	Force imposed on atom i from atom j [N]
\vec{G}	Reciprocal lattice vector $[m^{-1}]$
h	Planck's constant $[6.63\times 10^{-34}~{\rm m^2\cdot kg/s}]$
k	Thermal conductivity $[W/m \cdot K]$
k_d	Thermal conductivity of air in nanoporous thin films $[\mathrm{W}/\mathrm{m}{\cdot}\mathrm{K}]$
$k_{d,0}$	Thermal conductivity of bulk air $[\mathrm{W}/\mathrm{m}{\cdot}\mathrm{K}]$
k_B	Boltzmann constant $[1.38\times 10^{-23}~{\rm J/K}]$
K	Wavenumber $[m^{-1}]$
\vec{K}	Wavevector $[m^{-1}]$
Kn	Knudsen number
l	Phone mean free path [m]
L	Metallic wire length or size of a crystalline solid [m]
m	Mass [kg]
n	Number of atoms per unit volume of material $[m^{-3}]$
N	Total number of phonon modes
p	Pressure [Pa]
\vec{p}	Phonon momentum $[m \cdot kg/s]$
Р	Heating power [W]
q''	Heat flux $[W/m^2]$
\vec{r}	Atom trajectory [m]
R_e	Electrical resistance $[\Omega]$

t	Thickness [m]
Т	Temperature [K]
u	Thermal Energy $[J/m^3]$
U	Interatomic potential [J]
v_g	Group velocity [m/s]
V_{ω}	First harmonic voltage drop [V]
$V_{3\omega}$	Third harmonic voltage drop [V]

Symbols

α	Thermal diffusivity $[m^2/s]$
γ	Temperature coefficient of resistance of the metallic wire $[1/K]$
ΔT	Difference in temperature oscillation amplitudes [K]
\mathcal{D}	Phonon density of states
θ_D	Debye temperature [K]
θ_i	Characteristic temperature in the Cahill-Pohl thermal conductivity model [K]
λ	Wavelenth [m]
ρ	Density $[kg/m^3]$
σ	Diameter of gas molecules [m]
ω	Angular frequency [rad/s]
τ	Phonon relaxation time [s]
\hbar	Reduced Planck's constant $[1.054\times 10^{-34}~{\rm m^2\cdot kg/s}]$
Ψ	Porosity function

Subscripts

В	Refers to phonon-boundary scattering
cp	Refers to the coherent potential approximation
Callaway	Refers to the Callaway model
CP	Refers to the Cahill-Pohl thermal conductivity model
D	Refers to the Debye model or phonon-defect scattering

eff	Refers to effective properties
Eucken	Refers to the Eucken effective medium approximation
f	Refers to thin film
f + sub	Refers to thin film and substrate
i	Refers to transverse or longitudinal polarization
m	Refers to dense matrix properties
Russell	Refers to the Russell effective medium approximation
sub	Refers to substrate
U	Refers to Umklapp scattering
z	Refers to the z -direction in Cartesian coordinates

CHAPTER 3

Thermal Conductivity of Highly-Ordered Mesoporous Titania Thin Films

This chapter investigates the cross-plane thermal conductivity of highly-ordered amorphous and crystalline templated mesoporous titania thin films. The thermal conductivity was measured from 30 to 315 K using the 3ω method. Both sol-gel and nanocrystal-based films were synthesized by evaporation-induced self-assembly, with average porosity of 30% and 35%, respectively. The pore diameter ranged from 14 to 25 nm. The size of crystalline domains in polycrystalline mesoporous films was 12 to 13 nm while the nanocrystals in the nanocrystal-based film were 9 nm in diameter. The temperature dependence of the measured thermal conductivity is discussed as well as the effect of porosity, pore diameter, film thickness, crystallinity, and crystal size.

3.1 Introduction

A few studies reported the thermal conductivity of dense (non-porous) amorphous and crystalline TiO₂ films between 80 and 400 K [8, 11, 110, 111]. As for porous TiO₂ thin films, Choi *et al.* [27] measured the thermal conductivity of 250 nm thick amorphous templated hexagonal mesoporous TiO₂ thin films at room temperature. The authors concluded that the presence of nanoscale pores reduced the thermal conductivity by a factor 11 compared with that of non-porous crystalline TiO₂ [27]. Unfortunately, the authors did not report the film porosity and pore size. In addition, Feng *et al.* [112] reported the effective thermal diffusivity, cross-plane thermal conductivity, and density at room temperature of porous anatase TiO₂ thin films with thicknesses around 60 μ m made of randomly oriented nanofibers. Here also, porosity remained unknown. The effective thermal conductivity of these porous TiO₂ thin films was about one order of magnitude smaller than that of bulk dense anatase TiO₂ [112]. The authors indicated that the length and diameter of the nanofibers had no effect on the effective thermal conductivity [112]. Recently, Coquil *et al.* [5] reported the cross-plane thermal conductivity at room temperature of highly-ordered sol-gel and nanocrystal-based mesoporous TiO₂ thin films synthesized by evaporation-induced self-assembly, with average porosity of 30% and 35%, various values of pore diameter (7-30 nm), and film thickness (60-370 nm). The authors attributed the smaller thermal conductivity of amorphous thin films to the fact that heat was carried by very localized non-propagating vibrational modes. They also showed that the thermal conductivity can be tuned by controlling the porosity as well as the connectivity and size of the nanocrystals or of the crystalline domains. However, only room temperature results were reported.

The present study aims to (i) measure the effective cross-plane thermal conductivity of mesoporous TiO_2 thin films with various nanoscale architectures and (ii) investigate the effects of temperature, presence of pores, and crystallinity of the TiO_2 matrix over the temperature range from 30 to 315 K.

3.2 Method and Experiments

3.2.1 Sample Film Preparation

Synthesis of both non-porous and highly-ordered amorphous and crystalline cubic mesoporous TiO₂ thin films investigated in the present study were described in detail in Ref. [5]. The synthesis was based on calcination of polymer/titania composites produced by evaporation-induced self-assembly using the organic template poly(ethylene-co-butylene)block-poly(ethylene oxide) also referred to as KLE [113–115]. In addition, two types of mesoporous titania thin films were synthesized namely sol-gel derived films and nanocrystalbased (NC-based) films using methods reported by Fattakhova-Rohlfing *et al.* [113] and Brezesinski *et al.* [23], respectively. Finally, non-templated amorphous and crystalline TiO₂ thin films were prepared by a procedure similar to that used to synthesize the mesoporous sol-gel films but without any organic template. The non-templated films are also referred to as dense samples in order to distinguish them from the polymer-templated mesoporous ones. However, note that the sol-gel derived non-templated films were not fully "dense" but slightly porous [116]. Finally, the crystalline phase was anatase in all cases.

3.2.2 Characterization

Characterization of the films investigated in the present study has been reported in detail by Coquil et al. [5]. It included one- and two-dimensional small-angle X-ray scattering (1D-SAXS and 2D-SAXS), scanning and transmission electron microscopy (SEM and TEM), and wide-angle X-ray diffraction (WAXD) measurements [5]. In brief, Figures 3.1(a) and 3.1(b) show SEM micrographs of KLE-templated sol-gel amorphous and of crystalline mesoporous TiO_2 thin films, respectively [5]. These micrographs confirmed the highly-ordered mesoporous structure of the films. The KLE-templated sol-gel mesoporous TiO₂ thin films consisted of ellipsoidal pores of in-plane diameter 14 to 19 nm organized in body centered cubic (bcc) lattice with a porosity of 30%. Moverover, the KLE-templated sol-gel films showed similar pore dimensions in crystalline and amorphous states as also observed by Fattakhova-Rohlfing *et al.* [113]. Figures 3.1(c) and 3.1(d) respectively show SEM and bright field TEM micrographs of the disordered but macroscopically homogeneous architecture of NC-based mesoporous TiO_2 films made of anatase nanocrystals about 9 nm in size and featuring pores 17 to 25 nm in diameter. Note that the dense crystalline sol-gel type TiO_2 thin films featured crystalline domains about 30 nm in diameter. Table 3.1 summarizes the crystallinity, porosity, film thickness, pore diameter, wall thickness, and crystal size of the TiO_2 thin films investigated.

3.2.3 Experimental Setup

The cross-plane thermal conductivity of the highly-ordered amorphous and crystalline templated mesoporous titania thin films was measured between 30 and 315 K using the 3ω method [9,76]. A thin silicon nitride (Si_xN_y) layer was first deposited on the sample films by



Figure 3.1: SEM micrographs of KLE templated sol-gel derived (a) amorphous and (b) crystalline mesoporous TiO_2 , (c) SEM and (d) TEM micrographs of nanocrystal-based mesoporous TiO_2 thin films also templated using the large diblock copolymer KLE. [5].

plasma enhanced chemical vapor deposition (PECVD) in order to (i) protect the mesoporous structure of the samples and (ii) act as an electrically insulating layer. Meanwhile, a nitride layer with identical thickness was also deposited on a bare silicon substrate in the same batch as the samples and served as a reference. Figures 3.2(a) and 3.2(b) show schematics of cross-section views of a porous thin film sample and a reference sample, respectively. A gold or aluminum wire, as shown in Figure 2.1, was patterned on both the sample film of



interest passivated by a silicon nitride layer and the reference sample.

Figure 3.2: Schematics of the cross-section of (a) a porous thin film sample and (b) a reference sample.

This PECVD passivation process has also been used as an effective method to seal various porous thin films [97, 117–119]. In fact, Figure 3.3 shows a cross-section SEM micrograph of our highly-ordered mesoporous TiO_2 thin films. It establishes that only the open pores located at the surface of the film were filled with $\text{Si}_x \text{N}_y$. Their diameter represents a very small fraction of the film thickness.



Figure 3.3: Cross-section SEM micrograph of a typical mesoporous TiO_2 sample film protected with a PECVD $Si_x N_y$ layer.

Figure 3.4 shows a schematic of the experimental setup using the 3ω method. It consists of a thermal sub-system and an electrical sub-system.



Figure 3.4: Experimental setup used for thin film thermal conductivity measurement between 25 and 315 K.

Thermal Sub-System

The thermal sub-system consists of a cold finger cryostat (model ST100 from Janis Research Company, Inc.), a helium dewar, and a temperature controller (model 331s from Lake Shore Cryotronics, Inc.) used to control the temperature with ± 0.1 K accuracy. Figure 3.5(a) shows the actual ST-100 cryostat in the lab. The ST-100 cryostat imposes temperature from 25 to 315 K thanks to the Lakershore 331s temperature controller. In order to minimize sample temperature rise due to Joule heating in the metallic wire, cryogenic thermal grease was applied to the interface between the sample's substrate and the cryostat cold finger. The rise in sample temperature above the cryostat set temperature was estimated to be less than 5 K for T<100 K and less than 2 K for T>100 K. A radiation shield was included to reduce

heat losses by thermal radiation from the sample to the surrounding, as shown in Figure 3.5(b). Figure 3.5(c) shows an actual sample mounted on the sample holder. The cryostat is evacuated to a pressure less than 1 mtorr in order to minimize heat losses by convection use a two stage mechanical pumping system (7RVP by Janis Research Company).



Figure 3.5: Picture of the ST100 cryostat with sample mounted on. (a) ST100 cryostat, (b) aluminum radiation shield, (c) sample holder with sample mounted on.

Electrical Sub-System

The electrical sub-system consists of a sample holder [Figure 3.5(c)] by Janis Research Company, a lock-in amplifier (Stanford research system, SR830), a metallic wire patterned on top of the sample films, an electrical circuit and a computer for data acquisition. Figure 3.6(a) shows the metallic wire used in the actual experiment along with the location of the four pads numbered 1 to 4. Figure 3.6(b) shows the electrical circuit used to implement the 3ω method along with the nodes associated with the four pads shown in Figure 3.6(a). The lock-in amplifier served as (i) a multimeter to measure the voltage drop across the metallic wire, (ii) a function generator to generate a sinusoidal current, and (iii) a power supply to supply a bias voltage for the differential amplifiers (Analog devices, AD524) used in the electrical circuit.



Figure 3.6: (a) Schematic and photograph of the metallic heater and contact pads and (b) electrical circuit used for the 3ω method.

A metallic wire made of 10 nm thick chromium and 100-150 nm thick aluminum or gold was deposited on both the sample and the reference by a standard lift-off process. It was 30 μ m wide and 1 mm long. The metallic pattern was then connected to the measuring circuit using a wire bonding technique. To do so, one end of a bonding wire was first connected to the sample carrier by ultrasonic wire bonding. Then, the other end of the wire was carefully attached to the metallic pattern using silver epoxy. Finally, the sample and its carrier together were baked at 65°C for 4 hours to ensure good electrical conductivity.

The electrical circuit using the so-called common-mode-subtraction technique [9,69,120]. It was designed to measure the third harmonic component of the voltage drop $V_{3\omega}$ across the metallic wire and to achieve maximum signal to noise ratio. Moreover, it is essential to have a reference resistor whose resistance does not vary with temperature since the 3ω method relies on measuring small voltage fluctuations across the metallic wire. In the first harmonic mode, the A-B signal [Figure 3.6(b)] should be set as close to 0 V as possible, typically below 0.5 mV, by adjusting the reference resistance to match the patterned wire resistance.

3.2.4 Experimental Procedure

The measurement for nanoporous thin films can be divided into two steps. First, the temperature of the metallic heater was calibrated and its temperature-dependent electrical resistance $R_e(T)$ was measured. To do so, a small AC voltage (around 0.1 V_{rms}) was supplied to the metallic heater to measure its electrical resistance $R_e(T)$ between 25 and 315 K. Second, the cross-plane thermal conductivity of the sample film was measured under a given temperature. To do so, a large AC voltage (around 0.5 V_{rms}) was applied to the metallic heater at different frequencies. The third harmonic voltage drop $V_{3\omega}$ across the metallic heater was collected by a lock-in amplifier with a 2% relative uncertainty at each frequency. As suggested by Cahill [9], the frequency range was chosen such that (i) the in-phase component of the amplitude of $V_{3\omega}$ decreased linearly with the logarithm of frequency and (ii) the out-of-phase component of the amplitude of $V_{3\omega}$ was nearly independent of frequency. In the present study, the typical frequency range considered was from 0.4 to 2.0 kHz. The temperature oscillation amplitude ΔT was then determined from the third harmonic voltage $V_{3\omega}$ according to [9],

$$\Delta T = \frac{2V_{3\omega}R_e}{V_{\omega}\left(\mathrm{d}R_e/\mathrm{d}T\right)}\tag{3.1}$$

where V_{ω} is the applied first harmonic AC voltage while dR_e/dT is the derivative of the electrical resistance of the heater with respect to temperature.

A large contribution to the uncertainty of ΔT given by Equation (3.1) is due to the uncertainty associated with dR_e/dT . For small temperature range, a linear relationship between R_e and T can be used to fit the data [69]. However, large error is expected when fitting data with a linear function over a wide temperature range. Instead, the Bloch-Grüneisen (B-G) model [85] was used, in the present study, to fit $R_e(T)$ between 25 and 315



Figure 3.7: (a) Typical electrical resistance of an aluminum heater along with linear fitting (dash line) and the Bloch-Grüneisen model fitting (solid line) given by Equation (3.2) for $A = 10.62 \ \Omega, B = 45.17 \ \Omega, \text{ and } C = 337.8 \text{ K.}$ (b) The relative difference ε versus temperature. Here, $\varepsilon = [R_{e,fit}(T) - R_e(T)] / R_e(T)$, where $R_{e,fit}(T)$ is the fitted value at temperature T obtained either by linear fit or using the Bloch-Grüneisen model.

K as performed by Chen *et al.* [121]. The B-G model is expressed as [85],

$$R_{e,B-G}(T) = A + B\left(\frac{T}{C}\right)^5 \int_0^{C/T} \frac{x^5}{(e^x - 1)(1 - e^{-x})} \mathrm{d}x,$$
(3.2)

where A, B, and C are three empirical parameters. These parameters were obtained, for each film, by fitting Equation (3.2) to experimental data for $R_e(T)$ using the simplex method [122]. Figure 3.7(a) shows the typical electrical resistance of an aluminum heater as a function of temperature. It indicates that the fitted B-G model gave better prediction of the experimental data than linear curve fitting for $A = 10.62 \ \Omega$, $B = 45.17 \ \Omega$, and C = 337.8K. The relative difference ε between experimental measurement and prediction by the fitted model is defined as $\varepsilon = [R_{e,fit}(T) - R_e(T)]/R_e(T)$, where $R_{e,fit}(T)$ is the fitted value at temperature T obtained either by linear fit or using the B-G model. Figure 3.7(b) shows the relative differences ε for linear fitting and B-G model versus temperature. Here, ε associated with the B-G model was less than 0.5% for all temperatures. For the linear fit, ε was larger than 0.5% and reached up to 4% for T < 150 K. Finally, the derivative of the electrical resistance with respect to temperature dR_e/dT used in Equation (3.1) was calculated by applying centered difference method to the B-G fitted curve.



Figure 3.8: Example of amplitude of temperature oscillation per unit power $\Delta T_{ref}/P$ and $\Delta T_{tot}/P$ as a function of frequency at temperatures 66 K and 295 K.

The amplitude of temperature oscillations in the sample film ΔT_f was calculated by subtracting the amplitude of temperature oscillation of the reference nitride film ΔT_{ref} from that of the mesoporous film with the protective nitride film denoted by ΔT_{tot} [76], i.e.,

$$\Delta T_f = \Delta T_{tot} - \Delta T_{ref}.$$
(3.3)

Figure 3.8 shows typical amplitudes of temperature oscillation per unit heating power $\Delta T_{ref}/P$ and $\Delta T_{tot}/P$ as a function of frequency at temperatures 66 and 295 K, respectively. The difference in $\Delta T_f/P$ between the sample and the reference appeared to be independent of frequency. Finally, the effective cross-plane thermal conductivity k_f of the nanoporous thin film sample can be expressed as [76],

$$k_f = \frac{Pt_f}{2bL\Delta T_f} \tag{3.4}$$

where t_f is the thickness of the sample film while 2b and L are the width and length of the metallic heater, respectively. Note that the random error associated with k_f was estimated to be less than 0.005 W/m·K by performing at least three independent measurements for each temperature. Error propagation analysis was performed to estimate the overall uncertainty associated with the measured thermal conductivity $k_f(T)$ computed using Equations (3.1) to (3.4).

3.2.5 Validation

The experimental apparatus was first validated by measuring the thermal conductivity of high purity single crystal silicon substrate and thermally grown amorphous silicon dioxide (thermal oxide) films. Figure 3.9 compares the measured thermal conductivity of high purity single crystal silicon substrate as a function of temperature with data reported in the literature [6,7]. Good agreement (within 10%) was found between the present and reported data [6]. In addition, the thermal conductivity for B or Sb doped silicon reported by Lee and Cahill [7] were smaller than those measured in the present study. This can be attributed to phonon scattering by the dopant atoms.

Moreover, Figure 3.10 shows the thermal conductivity of 1.2 μ m thick thermal oxide film as a function of temperature between 30 and 315 K. The experimental uncertainty for each data point was estimated to be smaller than 0.05 W/m·K. The maximum and average relative difference between the present study and the previous results for 0.99 μ m thick thermal oxide [8] and bulk amorphous silica (Vitreosil) [9] were 9% and 6%, respectively. This also confirms that when the silica film is thicker than 1 μ m, the apparent thermal conductivity is approximately that of bulk silica [8,10]. The slight difference among different data sets could be attributed to the difference in silica density and composition (impurities).

Overall, the experimental setup and the associated analysis were in good agreement with



Figure 3.9: Measured thermal conductivity of high purity single crystal silicon substrate as a function of temperature along with data reported in the literature for high purity and Sb and B doped single crystal silicon [6,7].

experimental data reported in the literature for high purity single crystal silicon [6] and thermal oxide [8] between 30 and 315 K. Therefore, the experimental setup and procedure can be utilized to measure the thermal conductivity of the dense or nanoporous, amorphous or polycrystalline thin films in the present study.

3.3 Results and Discussion

3.3.1 Dense Amorphous and Polycrystalline Titania Thin Films

Experimental Results

Table 3.2 summarizes the thermal conductivity measured for dense and ordered mesoporous titania thin films at temperatures between 30 and 315 K. Figure 3.11 shows the measured



Figure 3.10: Measured thermal conductivity of 1.2 μ m thick thermal oxide film as a function of temperature between 30 and 315 K along with previously reported data [8–10].

thermal conductivity of sol-gel derived non-templated (referred to as dense) polycrystalline and amorphous TiO₂ thin films as a function of temperature between 30 and 315 K. The average experimental uncertainty for both films was about 14%. Figure 3.11 indicates that the thermal conductivity of the polycrystalline and amorphous dense films denoted by $k_d(T)$ increased monotonically with increasing temperature. By contrast, the thermal conductivity of bulk dense crystalline materials typically decreases with increasing temperature for temperatures larger than $T_{Debye}/10$ due to phonon Umklapp scattering [4]. Note that the Debye temperature T_{Debye} for anatase is about 500 K [123]. Therefore, the present observations suggest that phonon scattering by crystalline grains and film boundaries dominates over phonon Umklapp scattering in the polycrystalline dense TiO₂ film. In addition, the measured thermal conductivity of both polycrystalline and amorphous films varied as T^2 for low temperatures between 30 and 60 K. Moreover, the thermal conductivity of the polycrystalline film (sample 2) was about three times larger than that of the amorphous film (sample 1) for any given temperature. This was mainly due to the fact that, in amorphous materials, heat is transferred mainly by localized lattice vibrations as opposed to phonons with relatively long mean free path in crystalline materials [69].



Figure 3.11: Measured thermal conductivity of sol-gel derived non-templated (dense) amorphous and polycrystalline TiO_2 thin films as a function of temperature between 30 and 315 K along with previously reported data [11] and predictions by the Cahill-Pohl model [Equation (3.5)].

Figure 3.11 also shows the thermal conductivity of sputtered polycrystalline and amorphous TiO_2 thin films between 80 and 400 K reported by Lee *et al.* [11]. The sputtered polycrystalline TiO_2 thin film had average grain size of about 8 nm and film thickness between 0.5 and 2.0 μ m [11]. It is evident that the thermal conductivity of the sol-gel dense polycrystalline film (sample 2) was similar to that of the sputtered polycrystalline film [11]. However, the thermal conductivity of the sputtered amorphous film was about two times larger than that of the sol-gel dense amorphous film (sample 1). This difference suggests that these films may have different density and/or compositions caused by the very different synthesis processes. For example, dense titania thin films prepared by the sol-gel method usually have lower density than sputtered films [116]. In addition, sol-gel derived amorphous titania often contains additional hydroxyl groups, compared with sputtered titania [124], which result in the stoichiometry TiO_x with x > 2.

As discussed in Chapter 2, the thermal conductivity of a strongly disordered material as a function of temperature can be calculated by the Cahill-Pohl model as [89],

$$k_{CP}(T) = \left(\frac{\pi}{6}\right)^{1/3} k_B n^{2/3} \sum_{i=1}^{3} v_{g,i} \left(\frac{T}{\theta_i}\right)^2 \int_0^{\theta_i/T} \frac{x^3 e^x}{\left(e^x - 1\right)^2} dx.$$
 (3.5)

where $k_B = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant, n is the number of atoms per unit volume of material. Summation is performed over three polarizations including two transverse and one longitudinal polarizations with associated speed of sound $v_{g,i}$ and characteristic temperature $\theta_i = v_{g,i}(\hbar/k_B) \times (6\pi^2 n)^{1/3}$, where $\hbar = 1.054 \times 10^{-34} \text{ m}^2 \text{kg/s}$ is the reduced Planck's constant. The Cahill-Pohl model has been termed the minimum thermal conductivity model for amorphous and strongly disordered polycrystalline materials [4]. Here, the average speed of sound $v_g = 4140$ m/s for an atase TiO₂ was used for all three polarizations [123]. The atom number per unit volume was taken as $n = 2.94 \times 10^{28} \text{ m}^{-3}$ according to measurements by Lee *et al.* [11] for sputtered amorphous TiO_2 . As previously mentioned, the actual atom number per unit volume in dense sol-gel films may be smaller [116]. The minimum thermal conductivity of strongly disordered TiO_2 predicted by Equation (3.5) was also plotted in Figure 3.11 (dash line). It is evident that the minimum predictions by the model were close to the measured thermal conductivity of sol-gel dense amorphous TiO_2 thin film (sample 1). This could be attributed to its amorphous phase as well as to the small porosity resulting from the sol-gel process, as previously mentioned. As expected, the model predictions were smaller than k_d measured for all other dense TiO₂ thin films.



Figure 3.12: Ratio $k_d(T)/k_{CP}(T)$ as a function of temperature between 30 and 315 K for sputtered [11] and sol-gel derived dense TiO₂ thin films. $k_d(T)$ was shown in Figure 3.11 and $k_{CP}(T)$ was predicted from Equation (3.5).

In order to compare the temperature dependence of the measured thermal conductivity with that predicted by Equation (3.5), Figure 3.12 plots the ratio $k_d(T)/k_{CP}(T)$ as a function of temperature. It indicates that for T > 120 K, $k_d(T)/k_{CP}(T)$ was nearly independent of temperature for dense sputtered as well as for sol-gel amorphous and polycrystalline TiO₂ thin films. It establishes that the Cahill-Pohl model successfully captured the temperature dependence of the thermal conductivity of both amorphous and polycrystalline dense sol-gel films. On the other hand, for T < 120 K, the ratio $k_d(T)/k_{CP}(T)$ increased as temperature decreased. The discrepancy between the measured and predicted thermal conductivity at low temperatures was also observed by Cahill and Pohl [90] for amorphous silica. It was attributed to the fact that the Cahill-Pohl model does not include energy transport by phonons with long mean free path whose contributions become important at low temperatures in both amorphous and strongly disordered polycrystalline solids [90, 125].

3.3.2 Mesoporous Titania Thin Films

Figure 3.13 shows the measured thermal conductivity as a function of temperature for the amorphous and polycrystalline, sol-gel and NC-based, mesoporous TiO₂ thin films (samples 3 to 7), denoted by $k_f(T)$. The average experimental uncertainty was between 5 and 11% for all films between 30 and 315 K. Note that the thermal conductivity of the mesoporous TiO₂ thin films measured at room temperature agreed well with previous results reported by Coquil *et al.* [5]. This confirms their assumption that heat losses to the surroundings by conduction and convection were negligible in their experiments.

Sol-gel Amorphous Mesoporous TiO₂ Thin Films

Figure 3.13 indicates that the thermal conductivity of sol-gel amorphous mesoporous TiO_2 thin films (samples 3 and 4) increased with increasing temperature. It was less than half of that for the amorphous dense film, for all temperatures. The reduction in thermal conductivity of the amorphous mesoporous TiO_2 thin films was mainly due to the facts that (i) in amorphous materials heat is transferred by very localized non-propagating vibrational modes and (ii) the cross-sectional area for heat transfer through the film is reduced by the presence of the pores [69]. In addition, the thermal conductivity of sample 4 was slightly larger than that of sample 3 for all temperatures with a maximum absolute difference less than or comparable to the experimental uncertainty. This could be attributed to variations in morphology from one sample to another.

Moreover, the thermal conductivity of amorphous mesoporous TiO_2 thin films was proportional to T for temperature T < 60 K as opposed to T^2 for the corresponding dense film (sample 1). This could be due to the fact that the presence of mesopores reduces the



Figure 3.13: Measured thermal conductivity as a function of temperature between 30 and 315 K for polymer-templated sol-gel (samples 3 to 6) and NC-based (sample 7) mesoporous TiO_2 thin films.

contribution, to heat transfer, of phonon modes with long mean free path. This, in turn, makes the thermal conductivity less temperature dependent.

Finally, Figure 3.14 plots the ratios of the thermal conductivity $k_f(T)$ of samples 3 and 4 (Figure 3.13) to that of dense sample 1 denoted by $k_d(T)$ (Figure 3.11) as a function of temperature. They were found to be equal to 0.35 and 0.41 and independent of temperature between 60 and 315 K. This confirms the observations made by Shin *et al.* [117] on mesoporous amorphous SiO₂ films indicating that the presence of the pores in amorphous materials had a purely geometrical effect and did not affect the localized vibrational



Figure 3.14: Ratio of measured thermal conductivity of sol-gel derived KLE templated mesoporous films $k_f(T)$ (Figure 3.13) to that of the corresponding dense film $k_d(T)$ as a function of temperature between 30 and 315 K. Here, $k_d(T)$ was taken as (i) $k_d(T)$ measured for sample 1 in the case of samples 3 and 4 and (ii) $k_{d2}(T)$ given by Equation (3.8) in the case of samples 5 and 6.

modes. Then, the temperature dependence of $k_f(T)$ was captured by that of the continuous amorphous phase denoted by $k_d(T)$. Thus, for T > 60 K, the thermal conductivity of the amorphous mesoporous films $k_f(T)$ can be expressed as a function of $k_d(T)$ and a geometric parameter such as porosity f_v using some effective medium approximation. For T < 60K, the ratios increased with decreasing temperature. This is due to the fact that, at low temperatures, the thermal conductivity of the mesoporous amorphous films is less temperature dependent $(k_f \propto T)$ than that of the dense amorphous film $(k_d \propto T^2)$, as previously discussed.

Sol-gel Polycrystalline Mesoporous TiO₂ Thin Films

Figure 3.13 indicates that the sol-gel polycrystalline mesoporous TiO_2 thin films (samples 5 and 6) featured thermal conductivity approximately one third as large as that of the dense polycrystalline thin film (sample 2) from 30 to 315 K shown in Figure 3.11. This reduction can be attributed to phonon scattering by pores and by smaller crystalline domains. In fact, the crystalline domain size were 12 to 13 nm in sol-gel polycrystalline mesoporous films (samples 5 and 6) as opposed to 30 nm in their dense counterpart (sample 2). The difference in thermal conductivity between the two porous samples (5 and 6) was less than the experimental uncertainty for all temperatures.

Figure 3.13 shows that the thermal conductivity of sol-gel polycrystalline mesoporous TiO_2 thin films (samples 5 and 6) varied as $T^{1.5}$ for temperatures below 60 K as opposed to T^2 for the corresponding dense film (sample 2). In addition, the thermal conductivity of polycrystalline mesoporous TiO₂ thin films reached a constant value of about 1.0 W/m·K for temperatures larger than 300 K. This suggests that nearly all phonon modes were excited above 300 K. Note that such a plateau was not observed at high temperatures for the polycrystalline dense TiO₂ film.

The effect of the presence of the pores was further investigated by comparing the thermal conductivity of the polycrystalline mesoporous TiO_2 thin film with that of the equivalent dense film. To account for the effect of crystalline domain size, Smith and co-workers [93,126] expressed the total thermal resistance of polycrystalline material as the sum of the thermal resistance of the equivalent single crystal and that of all grain boundaries in series as,

$$\frac{1}{k_d(T)} = \frac{1}{k_{crystal}(T)} + \frac{R_{int}(T)}{d_g}$$
(3.6)

where $k_{crystal}$ is the thermal conductivity of bulk single crystal, R_{int} is the thermal resistance of a single grain boundary, and d_g is the average grain size. This model was adopted to predict the thermal conductivities k_{d1} and k_{d2} of bulk dense polycrystalline anatase TiO₂
with grain size $d_{g1} = 30$ nm and $d_{g2} = 13$ nm, respectively. Hence, the ratio k_{d2}/k_{d1} can be expressed as,

$$\frac{k_{d2}(T)}{k_{d1}(T)} = \frac{1 + k_{crystal}(T)R_{int}(T)/d_{g1}}{1 + k_{crystal}(T)R_{int}(T)/d_{g2}}$$
(3.7)

To the best of our knowledge, the thermal conductivity $k_{crystal}(T)$ of bulk single crystal anatase as a function of temperature is not available in the literature. However, the thermal conductivity of rutile, another polymorph of TiO₂, was reported between 1 and 400 K [10]. It decreases with increasing temperature above 15 K, and is 11.7 and 8.5 W/m·K at 300 K for bulk single crystal and polycrystalline rutile, respectively [10]. We expect it to be similar for anatase phase. In addition, the thermal resistance $R_{int}(T)$ of a crystalline grain boundary is typically on the order of $10^{-8} \text{ m}^2 \cdot \text{K/W}$ [126]. Therefore, for $d_g \sim 10 \text{ nm } k_{crystal}R_{int}/d_g$ is on the order of 10 at room temperature. For lower temperatures, this term should increase due to significant increase in $k_{crystal}(T)$ [10] and only moderate change in $R_{int}(T)$ [126]. Thus, as a first order approximation, the ratio $k_{d2}(T)/k_{d1}(T)$ simplifies as,

$$\frac{k_{d2}(T)}{k_{d1}(T)} = \frac{d_{g2}}{d_{g1}}.$$
(3.8)

Here, the thermal conductivity $k_{d2}(T)$ of dense polycrystalline TiO₂ with grain size $d_{g2}=13$ nm was calculated by substituting $k_{d1}(T)$ with measured data for sample 2 whose grain size was $d_{g1}=30$ nm. Figure 3.14 also plots the ratios of the thermal conductivity of samples 5 and 6 to that of k_{d2} as a function of temperature. Unlike for amorphous mesoporous samples, the ratios fluctuate with temperature and no clear trend was apparent. This can be attributed to the presence of the pores which affect the phonon dispersion and density of states possibly due to the quantum confinement effect [127].

Nanocrystal-Based Mesoporous TiO₂ Thin Film

Figure 3.13 shows that the thermal conductivity of the NC-based mesoporous TiO_2 thin film (sample 7) was 40% less than that of the sol-gel polycrystalline mesoporous thin films (samples 5 and 6). This was due to the facts that (i) the nanocrystals contacted each other over very small surface area with additional microporosity stemming from the space between them [5], (ii) the anatase nanocrystal size was 9 nm as opposed to 12-13 nm for the polycrystalline domain of sol-gel films, and (iii) NC-based mesoporous films had porosity of 35% instead of 30% for the sol-gel films. This poorly connected nanostructure caused significant phonon scattering at the interfaces between nanocrystals. On the other hand, the thermal conductivity of the NC-based film was about two times larger than that of sol-gel amorphous mesoporous films (samples 3 and 4) for all temperatures, despite their larger porosity. This can be attributed to the crystallinity of the NC-based mesoporous film.

In addition, the trend of thermal conductivity of the NC-based mesoporous TiO_2 thin film with respect to temperature indicates that both the crystalline nature of nanocrystals and the loosely connected porous structure affected its thermal conductivity. On the one hand, at low temperatures, its thermal conductivity was linearly proportional to temperature T as observed for amorphous mesoporous films (samples 3 and 4). On the other hand, its thermal conductivity reached a plateau beyond 300 K as observed for polycrystalline mesoporous films (samples 5 and 6), suggesting saturated phonon modes in the NC-based mesoporous TiO₂ film.

3.4 Conclusions

This chapter presented the preparation, characterization, and cross-plane thermal conductivity measurement of mesoporous TiO_2 thin films between 30 and 315 K. Amorphous and crystalline as well as sol-gel derived and nanocrystal-based mesoporous TiO_2 thin films were investigated. The following conclusions can be drawn:

The thermal conductivity of sol-gel derived TiO_2 thin films increased with increasing temperature. For amorphous and polycrystalline mesoporous TiO_2 thin films, conductivity at low temperatures was proportional to T and $T^{1.5}$, respectively, as opposed to T^2 for the corresponding non-templated (dense) films.

The Cahill-Pohl model for highly disordered materials captured the temperature dependence of the thermal conductivity of dense amorphous and polycrystalline TiO₂ thin films for T > 120 K.

The sol-gel amorphous mesoporous TiO_2 thin films had thermal conductivity less than

half of that of their dense counterpart. The thermal conductivity of amorphous dense and mesoporous films had similar temperature dependence for T > 60 K. This was due to the fact that the presence of the pores only reduces the cross-sectional area for heat transport without affecting the localized vibrational modes.

The thermal conductivity of sol-gel polycrystalline mesoporous TiO_2 thin films was three times smaller than that of their dense counterpart. This was mainly due to phonon scattering by pores and smaller crystalline domains (12-13 nm versus 30 nm). The thermal conductivity of polycrystalline dense and mesoporous films had different temperature dependence suggesting that the presence of the pores also affect the phonon dispersion and density of state in the polycrystalline matrix.

The NC-based mesoporous TiO₂ film had thermal conductivity about 40% less than that of the polycrystalline mesoporous films and two times larger than that of the amorphous mesoporous films. This was attributed to its particles' crystallinity with smaller crystal size (~9 nm), larger porosity (35%), and poor connections between individual anatase nanocrystals.

	Table 3	.1: Characte	eristics of the	mesoporous	titania thin films	investigated.	
Sample	Crystallinity	$\mathbf{Process}$	Porosity	Thickness	Pore diameter	Wall thickness	Crystal size
#			$f_v~(\pm~2\%)$	t_f (nm)	d (mm)	t_{wall} (nm)	(uu)
1	amorphous	sol-gel	$\%0\sim$	120	I	I	ı
7	$polycrystalline^+$	sol-gel	$\%0\sim$	150	I	I	30
က	amorphous	sol-gel	30%	250	14 to 19	8 to 12	ı
4	amorphous	sol-gel	30%	300	14 to 19	8 to 12	ı
ŋ	$polycrystalline^+$	sol-gel	30%	260	14 to 19	8 to 12	12 to 13
6	$polycrystalline^+$	sol-gel	30%	370	14 to 19	8 to 12	12 to 13
7	$polycrystalline^+$	NC-based*	35%	160	17 to 25	15 to 25	9
*Nanocr	ystal-based, ⁺ Crysta	alline phase is	s anatase				

Table 3.2: Measured thermal conductivity (in W/m·K) of dense and ordered mesoporous titania thin films at temperatures

between 30 and <u>315 K.</u>

H	k of der	ise films		k of m	y snorodose	llms	
(K)	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
30	1	I	0.051 ± 0.003	0.052 ± 0.003	0.10 ± 0.01	$0.10 {\pm} 0.01$	0.11 ± 0.01
36.5	0.12 ± 0.01	$0.33 {\pm} 0.03$	0.059 ± 0.003	0.060 ± 0.003	$0.14{\pm}0.01$	$0.18 {\pm} 0.01$	0.13 ± 0.01
44.5	0.17 ± 0.02	$0.53{\pm}0.05$	0.070 ± 0.004	0.077 ± 0.004	$0.20 {\pm} 0.01$	$0.22 {\pm} 0.01$	$0.18{\pm}0.02$
54.2	$0.23 {\pm} 0.03$	$0.76{\pm}0.06$	0.088 ± 0.004	0.10 ± 0.005	$0.30{\pm}0.02$	$0.30{\pm}0.01$	0.22 ± 0.02
66	$0.31 {\pm} 0.03$	$1.01 {\pm} 0.11$	0.11 ± 0.01	0.13 ± 0.01	$0.38{\pm}0.03$	$0.39{\pm}0.02$	$0.26{\pm}0.02$
80.4	$0.38 {\pm} 0.05$	$1.26 {\pm} 0.15$	$0.14{\pm}0.01$	0.16 ± 0.01	$0.50{\pm}0.04$	$0.49{\pm}0.03$	$0.32{\pm}0.03$
98	$0.47 {\pm} 0.06$	$1.53{\pm}0.18$	0.17 ± 0.01	$0.20{\pm}0.01$	$0.62{\pm}0.06$	$0.63{\pm}0.04$	$0.39{\pm}0.03$
119.3	$0.56 {\pm} 0.07$	$1.84{\pm}0.24$	$0.20 {\pm} 0.01$	$0.23 {\pm} 0.01$	$0.74{\pm}0.07$	$0.72{\pm}0.04$	$0.45{\pm}0.04$
145.4	0.66 ± 0.09	$2.18{\pm}0.31$	$0.24 {\pm} 0.01$	0.27 ± 0.01	$0.86 {\pm} 0.08$	$0.85{\pm}0.05$	$0.51{\pm}0.05$
177.1	$0.76 {\pm} 0.11$	$2.55 {\pm} 0.41$	0.27 ± 0.02	$0.32 {\pm} 0.02$	$0.93 {\pm} 0.09$	$0.91{\pm}0.06$	$0.56{\pm}0.05$
215.7	$0.87 {\pm} 0.14$	$2.84{\pm}0.48$	$0.31 {\pm} 0.02$	$0.36 {\pm} 0.02$	$0.99 {\pm} 0.10$	$0.95 {\pm} 0.06$	$0.59{\pm}0.06$
262.7	$0.97{\pm}0.17$	$3.06{\pm}0.58$	$0.34{\pm}0.02$	$0.40 {\pm} 0.02$	1.01 ± 0.10	0.98 ± 0.06	$0.62{\pm}0.06$
300	1.03 ± 0.19	$3.10{\pm}0.62$	$0.36 {\pm} 0.02$	0.42 ± 0.02	1.06 ± 0.11	0.99 ± 0.06	$0.61{\pm}0.06$
315	1.06 ± 0.20	$3.25{\pm}0.65$	$0.36 {\pm} 0.02$	$0.43{\pm}0.02$	1.03 ± 0.10	1.00 ± 0.06	$0.62 {\pm} 0.06$

Nomenclature

A	Fitting parameter in the Bloch-Grüneisen model $[\Omega]$
b	Half width of the metallic wire [m]
В	Fitting parameter in the Bloch-Grüneisen model $[\Omega]$
C	Fitting parameter in the Bloch-Grüneisen model [K]
d	Pore diameter [m]
d_g	Crystal grain size [m]
f_v	Porosity
k	Thermal conductivity $[W/m \cdot K]$
k_B	Boltzmann constant $[1.38\times 10^{-23}~{\rm J/K}]$
L	Length of the metallic wire [m]
n	Atomic number per unit volume $[m^{-3}]$
Р	Heating power [W]
R_e	Electrical resistance $[\Omega]$
R_{int}	Thermal resistance of a single grain boundary $[\mathrm{m}^2{\cdot}\mathrm{K}/\mathrm{W}]$
t	Thickness [m]
Т	Temperature [K]
v_g	Speed of sound [m/s]
V_{ω}	First harmonic voltage drop [V]
$V_{3\omega}$	Third harmonic voltage drop [V]

Symbols

ΔT	Difference in temperature oscillation amplitudes [K]
ε	Relative difference between measured results and prediction for ${\cal R}_e$
θ_i	Characteristic temperature in the Cahill-Pohl model [K]
λ	Wavelenth [m]
\hbar	Reduced Planck's constant $[1.054 \times 10^{-34} \text{ m}^2 \cdot \text{kg/s}]$

Subscripts

B-G	Refers to the Bloch-Grüneisen model
crystal	Refers to single crystal titania
CP	Refers to the Cahill-Pohl model
d	Refers to dense film
Debye	Refers to the Debye model
f	Refers to thin film
fit	Refers to fitted results using linear fitting or the Bloch-Grüneisen model
i	Refers to transverse or longitudinal polarization
ref	Refers to reference sample
rms	Refers to root mean square
SiN	Refers to silicon nitride layer
tot	Refers to sample film and silicon nitride layer
TiO_2	Refers to mesoporous titania thin film
wall	Refers to wall between two adjacent pores

CHAPTER 4

Thermal Conductivity of Pure Silica MEL and MFI Zeolite Thin Films

This chapter discusses the cross-plane thermal conductivity of pure silica zeolite (PSZ) MFI and MEL thin films measured using the 3ω method between 30 and 315 K. PSZ MFI thin films were *b*-oriented, fully crystalline, and had a 33% microporosity. PSZ MEL thin films consisted of MEL nanoparticles embedded in a non-uniform and porous silica matrix. They featured porosity, relative crystallinity, and particle size ranging from 40% to 59%, 23% to 47%, and 55 to 80 nm, respectively. The measured thermal conductivity of MFI and MEL zeolite films was compared with that of amorphous silica. Finally, the thermal conductivity of MFI zeolite was modeled as a function of temperature using the Callaway model.

4.1 Introduction

Several studies have reported the thermal conductivity of powdered zeolites [128–131]. Effects of temperature, filling gas, moisture, and pressure were investigated [128–131]. In addition, Greenstein *et al.* [13] and Hudiono *et al.* [132] measured thermal conductivity of PSZ MFI zeolite films with thickness ranging from 10 to 20 μ m and temperature varying from 150 to 450 K. The MFI films were synthesized by secondary growth through a seeded hydrothermal process on alumina substrates. The measured thermal conductivity of (*h0l*)-oriented PSZ MFI films varied from 1.0 to 1.4 W/m·K in the temperature range considered [132]. That of calcined and uncalcined *c*-oriented PSZ MFI films deposited on silicon substrates was found to range from 0.75 to 1.1 W/m·K and 1.0 to 1.6 W/m·K, respectively [13]. More recently, Coquil *et al.* [12] measured room temperature thermal conductivity of PSZ MFI and MEL zeolite thin films. The MFI thin films were *b*-oriented, fully crystalline, and had a porosity of 33%. The MEL thin films featured porosity, relative crystallinity, and particle size ranging from 40% to 59%, 23% to 47%, and 55 to 80 nm, respectively. The authors found the thermal conductivity to be around 1.02 ± 0.10 W/m·K for all films despite their different porosity, relative crystallinity, and nanoparticle size.

4.2 Method and Experiments

4.2.1 Sample Film Preparation

Synthesis of PSZ MFI and MEL thin films investigated in the present study were previously described in detail [12, 46, 51]. MFI thin films were synthesized by *in situ* crystallization and were *b*-oriented. The MEL films were prepared by spin coating a zeolite nanoparticle suspension onto silicon substrates. The MEL suspension was synthesized by a two-stage process [46]. The first stage consisted of a 2 days heating and stirring of a tetraethylorthosilicate (TEOS) based solution at 80°C resulting in a MEL nanoparticle suspension. The second stage corresponded to the growth of the MEL nanoparticles from the same solution in a convection oven at 114°C. Finally, MEL thin films were obtained by spincoating the solution onto silicon substrates. Both relative crystallinity and nanoparticle size of the PSZ MEL increased as the second stage synthesis time increased. Here, the relative crystallinity is defined as the ratio of the micropore volume to the micropore volume of a fully crystalline PSZ MEL microcrystal [46]. Four different sets of MEL films corresponding to four different second stage synthesis times (15, 18, 21 and 24 hours) were studied. Note that all the MEL and MFI thin films were made hydrophobic by vapor-phase silylation with trimethylchlorosilane as described in Ref. [46].

4.2.2 Characterization

Detailed characteristics of the resulting PSZ MFI and MEL thin films have been reported in the literature [46,51,133,134]. Table 4.1 summarizes the characteristics of five types of PSZ MFI and MEL thin films investigated. Figure 4.1(a) shows a SEM image of an *in situ* PSZ



Figure 4.1: SEM micrographs of (a) *in situ* PSZ MFI and (b) spin-on MEL thin films. Insets show (a) the MFI framework viewed down the *b*-axis and (b) the MEL framework viewed down the *a*-axis [12].

MFI film (type 1) consisting of well-intergrown MFI crystals along with an inset showing the MFI framework viewed down the *b*-axis [12]. Figure 4.1(b) shows a SEM image of a spin-on PSZ MEL film (type 5) consisting of MEL nanoparticles embedded in a nonuniform, disordered, and porous silica matrix along with an inset showing the MEL framework viewed down the *a*-axis [12]. In addition, unlike the MFI thin film, the MEL thin films featured also a mesoporosity corresponding to the volume fraction occupied by mesopores 2.3 to 2.6 nm in diameter [135]. These mesopores were located between the disordered silica matrix and the MEL nanoparticles [136].

4.2.3 Thermal Conductivity Measurement

The cross-plane thermal conductivity of PSZ thin films was measured using the 3ω method [9,76]. The principles, experimental apparatus, experimental procedure, and validation of the method have already been described in Chapter 3. The experimental uncertainty typically varied from 5% to 10% corresponding to 95% confidence interval. The thermal conductivity of two different samples for each type of film listed in Table 4.1 was measured between 30 and 315 K. The measurements agreed within 10% of each other. In addition, the film thickness had negligible effect on the measured data. This can be attributed to the fact that phonon scattering by nanopores and crystal grain boundary dominated over phonon scattering by film boundary in PSZ films.

4.3 Physical Modeling

Finally, thermal conductivity of the PSZ MFI film was modeled using the following Callaway model as discussed in Chapter 2 [87],

$$k = \frac{k_B}{2\pi^2 v_g} \left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\theta_D/T} \tau_{eff}(\omega) \frac{x^4 e^x}{(e^x - 1)^2} dx,$$
(4.1)

where k_B is the Boltzmann constant, \hbar is the reduced Planck's constant, θ_D is the Debye temperature for MFI zeolite reported to be 377.6 K [137], $\tau_{eff}(\omega)$ is the effective phonon relaxation time, and v_g is the average effective sound velocity in MFI reported to be 3683 m/s [138]. The variable x is related to the phonon frequency ω and is equal to $\hbar\omega/k_BT$. Note that Equation (4.1) was obtained by using the Debye dispersion relation and density of states and ignoring the effect of phonon polarization as discussed in Ref. [139].

The effective phonon relaxation time τ_{eff} is related to the relaxation times for defect scattering τ_D , Umklapp scattering τ_U , and boundary scattering τ_B via the Matthiessen's rule as [87],

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_D} + \frac{1}{\tau_U} + \frac{1}{\tau_B}.$$
(4.2)

Defect scattering refers to phonon scattering by point defects such as inclusion of impurity atoms or lattice vacancies [4]. Boundary scattering corresponds to phonon scattering by the film boundaries as well as by micropores. Here, τ_D , τ_U , and τ_B were expressed as [4,132],

$$1/\tau_D = A\omega^4, \ 1/\tau_U = BT\omega^2 \exp(-\theta_D/3T), \text{ and } 1/\tau_B = v_g/l_B,$$
 (4.3)

where A and B are empirical constants, and l_B is the effective phonon mean free path (MFP) for boundary scattering.

4.4 Results and Discussion

4.4.1 Experimental Results

Table 4.2 summarizes the thermal conductivity measured for PSZ MFI and MEL thin films at temperatures between 30 and 315 K. Figure 4.2 shows the measured thermal conductivity of the PSZ MFI and MEL zeolite thin films as a function of temperature, along with data reported in the literature for calcined and uncalcined MFI zeolite [13] and amorphous silica [7]. The four MEL thin films differ from one another by their relative crystallinity. The inset shows a close view for the measured data for temperature T > 150 K in linear scale. The thermal conductivity of the *in situ* MFI film increased from 0.05 to 1.2 W/m K as temperature increased from 30 to 315 K. In addition, it was about 10% to 15% larger than that of calcined MFI zeolite measured by Greenstein *et al.* [13] between 150 and 315 K. However, the thermal conductivity of uncalcined MFI [13] was about 20% to 40% larger than that measured in the present study [13]. This was likely due to the fact that the uncalcined films measured by Greenstein *et al.* [13] were denser (2.1 g/cm^3) than the *in situ* MFI film (1.7 g/cm^3) investigated in the present study. Moreover, the measured thermal conductivity of our MFI films was comparable to or smaller than that of the amorphous silica [7] despite its crystalline nature. In fact, the MFI films had microporosity of about 33% due to the presence of subnanometer pores within the crystalline structures. Its thermal conductivity was thus greatly reduced by phonon scattering by micropores.



Figure 4.2: Measured thermal conductivity of PSZ MFI and MEL zeolite thin films as a function of temperature from 30 to 315 K, along with data reported in the literature for calcined and uncalcined MFI zeolite [13] and amorphous silica [7]. The blue line indicates calculated thermal conductivity using the Callaway model [Equation (4.1)]. The inset shows a close view for the measured data for temperatures T > 150 K in linear scale.

In addition, Figure 4.2 indicates that all measured thermal conductivity k was linearly proportional to T^n with n varying from 2 to 2.3 for temperature T < 60 K. At low temperatures, strongly disordered materials typically follows $k \propto T^2$ while for crystalline materials $k \propto T^3$ [4]. The present results can be attributed to the fact that the MFI and MEL films featured crystalline nanostructures which were highly disordered due to the large surface area of pores and nanocrystals. Furthermore, the inset in Figure 4.2 shows that the thermal conductivity of the PSZ MEL thin films was slightly smaller than that of the PSZ MFI thin film. This is due to the fact that the MEL thin films had larger porosity and were "partially" crystalline, consisting of crystalline nanoparticles embedded in amorphous silica matrix. Moreover, the thermal conductivity of MEL thin films increased slightly when the MEL relative crystallinity and particle size increased from 23% to 44% and 55 to 70 nm, respectively. However, it remained nearly unchanged when the relative crystallinity and particle size further increased beyond 44% and 70 nm. Then, the effects of increased relative crystallinity and particle size were compensated by the simultaneous increase in porosity.

4.4.2 Modeling Results

By analogy with other studies [4, 13, 130, 132, 140], the parameters $A = 1.38 \times 10^{-42} \text{ s}^3$, $B = 4.24 \times 10^{-21} \text{ s/K}$, and $l_B = 0.95 \text{ nm}$ in Equation (4.3) were obtained by fitting the predictions of Equations (4.1) to (4.3) to the experimental data over the entire temperature range explored.

Figure 4.2 shows that the calculated thermal conductivity from Equations (4.1) to (4.3) agreed within 6% of the experimental data for the PSZ MFI film for all temperatures between 30 and 315 K. It establishes that using the Debye dispersion relation instead of the complete phonon dispersion was sufficient to predict the thermal conductivity of MFI zeolite films. In addition, phonon boundary scattering was found to dominate over phonon Umklapp scattering in MFI zeolite as discussed in the literature [12,13,130,132]. In fact, the predicted thermal conductivity was insensitive to the Umklapp scattering relaxation time τ_U since $\tau_U \gg \tau_B$ and $\tau_U \gg \tau_D$ for all temperatures considered and all phonon frequencies up to the Debye cut-off frequency of $\omega_D/2\pi = 8$ THz. Similar conclusions were reached by Hudiono *et al.* [132] and Greenstein *et al.* [140] for MFI and LTA zeolite between 150 and 450 K.

Moreover, phonon defect scattering should be considered along with boundary scattering in order to accurately predict the thermal conductivity of the MFI films particularly at high temperatures. This was due to the fact that defect scattering strongly affects high frequency phonons $(1/\tau_D \propto \omega^4)$ which contribute significantly to energy transport particularly at high temperatures [4]. At low temperatures, however, defect scattering was less important and boundary scattering dominated.

Finally, the fitted phonon boundary scattering MFP $l_B = 0.95$ nm was comparable with the distance between two adjacent micropores or the wall thickness. In fact, the lattice constant of MFI zeolite was reported to be about 2 nm along both *a*- and *b*- axis [141]. Considering the pore width of 0.55 nm along the *a*-axis and 0.53 nm along the *b*-axis [46], the wall thickness was estimated to be about 1.5 nm. Note that Hudiono *et al.* [132] reported a fitted value of $l_B = 4.8$ nm for MFI zeolite, also comparable with the wall thickness. The difference between l_B and MFI wall thickness may be attributed to the semi-empirical relaxation time models as well as the differences between Debye and actual phonon dispersion and density of states in MFI zeolite.

4.5 Conclusions

This chapter reported preparation, characterization, and temperature dependent cross-plane thermal conductivity of PSZ MEL and MFI thin films. Despite their crystallinity, MFI thin films were found to have thermal conductivity comparable to or smaller than that of amorphous silica due to strong phonon scattering by micropore boundaries. For PSZ MEL films, effects of increased relative crystallinity and size of MEL nanoparticle on the thermal conductivity were compensated by the simultaneous increase in porosity. Finally, the thermal conductivity for MFI films was successfully modeled using the Callaway model based on the Debye approximation. Umklapp scattering had negligible effect on the predicted thermal conductivity. Instead, phonon boundary scattering dominated for all temperatures while defect scattering was important at high temperatures.

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		Second	MEL particle		LOTAL	Micropore	BET surface	Micropore		Kelative
Sample		stage	size	Porosity	pore vol.	vol.	area	area	Thickness	$\operatorname{crystallinity}$
type	Structure	duration (h)	$(\pm 1 \text{ nm})$	$(\pm 2\%)$	$(\mathrm{cm}^2\mathrm{g}^{-1})$	$(\mathrm{cm}^3\mathrm{g}^{-1})$	$(m^2 g^{-1})$	$(\mathrm{m}^2\mathrm{g}^{-1})$	$(\pm 10 \text{ nm})$	$(\pm 2\%)$
1	MFI	I		$33\%^1$	0.19^{2}	0.19^{2}	457^{2}	457^{2}	320	100%
2	MEL	15	55	40%	0.60^{3}	0.033^{3}	691^{3}	86^{3}	350	$23\%^3$
3	MEL	18	09	45%	0.70^{3}	0.048^{3}	750^{3}	119^{3}	300	$33\%^3$
4	MEL	21	20	58%	0.80^{3}	0.060^{3}	852^{3}	143^{3}	280	$44\%^3$
5	MEL	24	80	59%	0.83^{3}	0.068^{3}	889^{3}	149^{3}	330	$47\%^3$
¹ From I	Flanigen <i>et a</i>	<i>L</i> [133]								
2 From 2	Tang et al.	[34]								

Table 4.1: Characteristics of the synthesized PSZ MFI and MEL thin films.

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³Interpolated from Li *et al.* [46]

Т	k of PSZ MFI		k of PS	Z MEL	
(K)	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
30	$0.074{\pm}0.005$	$0.053 {\pm} 0.003$	$0.057 {\pm} 0.004$	$0.067 {\pm} 0.005$	$0.075 {\pm} 0.006$
36.5	$0.12{\pm}0.01$	$0.092{\pm}0.006$	$0.10{\pm}0.01$	$0.11{\pm}0.01$	$0.12{\pm}0.01$
44.5	$0.18{\pm}0.01$	$0.15 {\pm} 0.01$	$0.17 {\pm} 0.01$	$0.19{\pm}0.01$	$0.19{\pm}0.01$
54.2	$0.28{\pm}0.02$	$0.23 {\pm} 0.02$	$0.26{\pm}0.02$	$0.28{\pm}0.02$	$0.29{\pm}0.02$
66	$0.41 {\pm} 0.03$	$0.33 {\pm} 0.01$	$0.36{\pm}0.02$	$0.39{\pm}0.03$	$0.39{\pm}0.03$
80.4	$0.54{\pm}0.04$	$0.43 {\pm} 0.03$	$0.46{\pm}0.03$	$0.51 {\pm} 0.04$	$0.52{\pm}0.04$
98	$0.66 {\pm} 0.04$	$0.52{\pm}0.03$	$0.55{\pm}0.04$	$0.61{\pm}0.05$	$0.61{\pm}0.05$
119.3	$0.77{\pm}0.05$	$0.62{\pm}0.04$	$0.64{\pm}0.04$	$0.72 {\pm} 0.06$	$0.69{\pm}0.05$
145.4	$0.86{\pm}0.06$	$0.69 {\pm} 0.05$	$0.73 {\pm} 0.05$	$0.81{\pm}0.07$	$0.78{\pm}0.06$
177.1	$0.95{\pm}0.07$	$0.76 {\pm} 0.06$	$0.80{\pm}0.06$	$0.89{\pm}0.08$	$0.86{\pm}0.07$
215.7	$1.03 {\pm} 0.08$	$0.83 {\pm} 0.06$	$0.88{\pm}0.07$	$0.96{\pm}0.09$	$0.93{\pm}0.08$
262.7	$1.09{\pm}0.08$	$0.89{\pm}0.07$	$0.93{\pm}0.07$	$1.02 {\pm} 0.10$	$1.00 {\pm} 0.09$
293	$1.13{\pm}0.09$	$0.93{\pm}0.07$	$0.97{\pm}0.08$	$1.05 {\pm} 0.11$	$1.04{\pm}0.09$
315	$1.14{\pm}0.09$	$0.94{\pm}0.07$	$0.99{\pm}0.08$	$1.07 {\pm} 0.11$	$1.05 {\pm} 0.09$

Table 4.2: Measured thermal conductivity (in $W/m \cdot K$) of PSZ MFI and MEL thin films.

Nomenclature

A	Fitting parameter in defect scattering relaxation time model $[s^3]$
В	Fitting parameter in Umklapp scattering relaxation time model $[\mathrm{s}/\mathrm{K}]$
k	Thermal conductivity $[W/m \cdot K]$
k_B	Boltzmann constant $[1.38\times 10^{-23}~{\rm J/K}]$
l	Phone mean free path [m]
T	Temperature [K]
v_g	Speed of sound [m/s]

Symbols

$ heta_D$	Debye temperature [K]
λ	Wavelenth [m]
τ	Phonon relaxation time [s]
ω	Frequency [rad/s]
\hbar	Reduced Planck's constant $[1.054\times 10^{-34}~{\rm m^2\cdot kg/s}]$

Subscripts

В	Refers to phonon-boundary scattering
D	Refers to phonon-defect scattering
eff	Refers to effective properties
f	Refers to thin film
U	Refers to Umklapp scattering

CHAPTER 5

Thermal Conductivity of Mesoporous Nanocrystalline Silicon Thin Films

The present chapter reports the cross-plane thermal conductivity of ordered mesoporous nanocrystalline silicon thin films between 25 and 315 K using the 3ω method. The films were produced by evaporation induced self-assembly of mesoporous silica followed by magnesium reduction. The porosity, average crystallite size, pore diameter, and film thickness were about 30%, 13 nm, 16-18 nm, and 140-340 nm, respectively. Their effects as well as the effect of temperature on the thermal conductivity were systematically investigated. A physical model based on kinetic theory and the coherent potential effective medium approximation was used to predict the measured thermal conductivity for all temperatures. The dominant phonon scattering mechanisms in these nanostructured silicon films were identified.

5.1 Introduction

5.1.1 Measurements

Drost *et al.* [142] reported the thermal conductivity of nanoporous silicon made by electrochemical etching of bulk single crystal silicon. The film thickness and porosity were 10 μ m and 40-53%, respectively. However, pore size was not specified. The measured thermal conductivity was 1.2 and 1.75 W/m·K for p-type and n-type nanoporous silicon at room temperature, respectively. Several other experimental studies reported the thermal conductivity of electrochemically etched porous silicon films measured using the photoacoustic method [143–146]. The film thickness and the porosity ranged from tens to hundreds of micrometers and from 20% to 75%, respectively. The pores were usually cylindrical and perpendicular to the film substrate, with diameter ranging from tens to hundreds of nanometers [143–146]. In addition, Périchon *et al.* [147] reported the thermal conductivity of 50 μ m thick porous silicon film with 50% porosity measured using micro-Ramam scattering method at room temperature. However, the pore size was not reported. Wolf and Brendel [148] measured the in-plane thermal conductivity of porous silicon free standing films using a lock-in thermography technique. The sample thickness, porosity, and pore size were 3 to 27 μ m, 27% to 66%, and about 0.1 μ m, respectively [148]. Moreover, Gomès *et al.* [149] measured the thermal conductivity of electrochemically etched mesoporous silicon thin films with thickness ranging from 38 nm to 7.2 μ m, porosity from 30% to 80%, and crystallite size from 10 to 20 nm using scanning thermal microscopy [150, 151]. Note that, in all previously mentioned studies, the thermal conductivity was measured at room temperature and was about two orders of magnitude smaller than that of bulk single crystal silicon equal to 148 W/m·K [14].

In terms of temperature dependent studies of porous silicon, Gesele *et al.* [57] measured the cross-plane thermal conductivity of electrochemically etched porous silicon films between 35 and 315 K using the 3ω method. The film thickness, porosity, and crystallite size were about 21 to 46 μ m, 64% to 89%, and 1.7 to 9 nm, respectively [57]. The measured thermal conductivity typically ranged from 0.01 to 0.8 W/m·K and increased with increasing temperature [57]. Song and Chen [152] measured the in-plane thermal conductivity of macroporous silicon films from 50 to 300 K. The through-film cylindrical pores were periodically arranged and fabricated using photolithography. The film thickness, porosity, and pore size varied from 4 to 7 μ m, 17% to 26%, and 2 to 10 μ m, respectively. More recently, Hopkins *et al.* [153] reported the room temperature cross-plane thermal conductivity of 500 nm thick silicon films with etched through-film cylindrical pores arranged in a two-dimensional simple cubic lattice. The pore diameter and porosity varied from 300 to 400 nm and from 20% to 28%, respectively. The reduction in thermal conductivity was attributed to phonon boundary scattering as well as phonon confinement effect [153].

Finally, Wang *et al.* [15] reported the cross-plane thermal conductivity of nanocrystalline silicon films about 1 mm thick prepared using a current activated and pressure assisted densification technique. The porosity and the average grain size varied from 0 to 17% and

from 64 to 550 nm, respectively. The measured thermal conductivity showed a temperature dependence of $k \propto T^2$ at low temperatures. The author developed a frequency dependent relaxation time model for phonon-grain boundary scattering to accurately predict thermal conductivity of nanocrystalline silicon over a wide range of temperatures.

Most porous silicon films investigated in previous studies were made by electrochemical etching with cylindrical pores and branches. Their sizes were usually on the order of a few to tens of micrometers [154]. Non-close-packed crystalline silicon colloidal nanostructures have also been synthesized using laser-induced transient melt process and porous silicon in sub-micron scale can be produced [155]. Recently, ordered mesoporous silicon films with closely packed pores were produced from mesoporous silica framework using a combination of evaporation induced self-assembly and magnesium reduction [156]. This method enables one to tune the porosity as well as the pore size and spatial arrangement of the mesoporous materials, and in turn, their thermophysical properties [156].

5.1.2 Modeling

Kinetic Theory Model

Based on kinetic theory and relaxation time approximation, thermal conductivity of crystalline materials is expressed as [4],

$$k_m(T) = \frac{1}{3} \sum_{i=1}^{3} \int_K \hbar \omega_i(K) \mathcal{D}_i(K) \frac{\partial f_{BE,i}(K)}{\partial T} v_{g,i}^2(K) \tau_{eff,i}(K) dK,$$
(5.1)

where k_m is the solid matrix thermal conductivity, subscript *i* represents the longitudinal or the transverse polarizations, *K* is the wavenumber, $\omega_i(K)$ is the angular frequency, $\hbar = 1.054 \times 10^{-34} \text{ m}^2 \text{kg/s}$ is the reduced Planck's constant, $\mathcal{D}_i(K) = K^2/2\pi^2$ is the phonon density of states, $f_{BE,i}(K)$ is the Bose-Einstein distribution given by $f_{BE,i}(K) =$ $1/[\exp(\hbar\omega_i(K)/k_BT) - 1]$ where $k_B = 1.38 \times 10^{-23} \text{ J/K}$ is the Boltzmann constant, $v_{g,i} =$ $d\omega_i(K)/dK$ is the phonon group velocity, and $\tau_{eff,i}(K)$ is the total effective phonon scattering relaxation time [4]. Note that the summation is over one longitudinal (*i* = 1) and two transverse polarizations (*i* = 2, 3). A fourth order polynomial dispersion relation for silicon was suggested by Hopkins etal. [96] and given by,

$$\omega_i(K) = a_i K + b_i K^2 + c_i K^3 + d_i K^4, \qquad (5.2)$$

The authors determined the coefficients a_i , b_i , c_i , and d_i by fitting Equation (5.2) to the measured dispersion relation for bulk silicon in the [100]-direction [157]. For the longitudinal polarization, they were reported to be $a_1 = 8350 \text{ m/s}$, $b_1 = 2.94 \times 10^{-8} \text{ m}^2/\text{s}$, $c_1 = -3.53 \times 10^{-17} \text{ m}^3/\text{s}$, and $d_1 = 1.37 \times 10^{-27} \text{ m}^4/\text{s}$ while for the transverse polarizations they were $a_2 = a_3 = 6090 \text{ m/s}$, $b_2 = b_3 = -1.86 \times 10^{-7} \text{ m}^2/\text{s}$, $c_2 = c_3 = -3.36 \times 10^{-17} \text{ m}^3/\text{s}$, and $d_2 = d_3 = 1.94 \times 10^{-27} \text{ m}^4/\text{s}$ [96]. Integration over K is typically truncated up to a cut-off wavenumber $K_{max} = 1.2 \times 10^{10} \text{ m}^{-1}$ [96]. This corresponds to cut-off frequencies $\omega_{max,1} = 71.6 \text{ Trad/s}$ and $\omega_{max,2} = \omega_{max,3} = 28.3 \text{ Trad/s}$.

For bulk crystalline silicon, the total phonon relaxation time $\tau_{bulk,i}$ for polarization *i* can be related to the relaxation time for Umklapp scattering $\tau_{U,i}$, defect scattering $\tau_{D,i}$, and boundary scattering $\tau_{B,i}$ via the Matthiessen's rule as [4],

$$\frac{1}{\tau_{bulk,i}} = \frac{1}{\tau_{U,i}} + \frac{1}{\tau_{D,i}} + \frac{1}{\tau_{B,i}},\tag{5.3}$$

where the relaxation times $\tau_{U,i}$, $\tau_{D,i}$, and $\tau_{B,i}$ are given by [96, 158],

$$1/\tau_{U,i} = BT\omega_i^2(K)\exp(-C/T), \ 1/\tau_{D,i} = D\omega_i^4(K), \text{ and } 1/\tau_{B,i} = v_{g,i}(K)/E.$$
 (5.4)

Here, the coefficients B, C, D, and E are fitting parameters. Furthermore, for nanocrystalline silicon, additional phonon scattering by crystallite grain boundaries becomes important. Then, the total relaxation time for nanocrystalline silicon $\tau_{NC,i}$ can be simply expressed as,

$$\frac{1}{\tau_{NC,i}} = \frac{1}{\tau_{bulk,i}} + \frac{1}{\tau_{grain,i}},\tag{5.5}$$

where $\tau_{grain,i}$ is the relaxation time for phonon scattering by crystallite grain boundaries.

A commonly used model suggests that $\tau_{grain,i}$ can be expressed as $1/\tau_{grain,i} = v_{g,i}/d_{cryst}$ where d_{cryst} is the crystallite size [4]. This model is based on two assumptions: (i) the effective phonon mean free path is limited by the crystallite size and (ii) phonon scattering by grain boundaries is frequency independent or "gray" [15]. However, Wang *et al.* [15] recently indicated that a frequency dependent model was required in order to accurately predict thermal conductivity of nanocrystalline silicon. This model was given by [15],

$$\frac{1}{\tau_{grain,i}} = \frac{v_{g,i}}{\alpha d_{cryst}(0.7\omega_{max,i}/\omega_i)},\tag{5.6}$$

where α is a fitting parameter accounting for the effect of grain boundary transmission and varies between 0 and 1. Smaller value of α corresponds to lower phonon transmission through grain boundaries resulting in smaller thermal conductivity [15].

Finally, the effect of porosity on thermal conductivity of mesoporous silicon should be accounted for by using some effective medium approximations (EMAs) [96,159], as discussed in Chapter 2. Note that the pores in mesoporous silicon were so small that their thermal conductivity can safely be neglected as explained in Refs. [92,93]. Here, the coherent potential model will be used which expresses the effective thermal conductivity k_{eff} as [76,98],

$$k_{eff} = k_m \Psi_{cp}(f_v) = k_m (1 - 1.5 f_v).$$
(5.7)

where f_v and k_m are the porosity and thermal conductivity of the solid matrix, respectively.

Minimum Thermal Conductivity Model

As an alternative to the kinetic theory model [Equations (5.1) to (5.7)], the minimum thermal conductivity of strongly disordered material $k_{m,min}$ can be estimated using the following Cahill Pohl model as discussed in Chapter 2 [89],

$$k_{m,min}(T) = \left(\frac{\pi}{6}\right)^{1/3} k_B n^{2/3} \sum_i v_{g,i} \left(\frac{T}{\theta_i}\right)^2 \int_0^{\theta_i/T} \frac{x^3 e^x}{\left(e^x - 1\right)^2} dx,$$
(5.8)

where $n = 5.02 \times 10^{28} \text{ m}^{-3}$ is the atomic number density of crystalline silicon and θ_i is a characteristic temperature expressed as $\theta_i = v_{g,i}(\hbar/k_B)(6\pi^2 n)^{1/3}$ [89]. This model has been termed the minimum thermal conductivity model and applies to amorphous and strongly disordered polycrystalline materials [4].

The present study aims to systematically investigate the effects of temperature, film thickness, and copolymer template on the thermal conductivity of ordered mesoporous nanocrystalline silicon thin films. First, sample film preparation and characterization were described. Then, the effective thermal conductivity measured using the 3ω method was reported from 25 to 315 K. Finally, theoretical modeling was developed by combining the kinetic theory model and the coherent potential EMA. The model predictions were compared with experimental data.

5.2 Method and Experiments

5.2.1 Sample Film Preparation

The synthesis of ordered mesoporous silicon thin films similar to the ones investigated in the present study was previously described in detail in Ref. [156]. Briefly, evaporation induced self-assembly (EISA) using sol-gel silica precursors and a diblock copolymer template was used to produce the precursor material – an ordered mesoporous silica film [69]. Mesoporous silicon was produced from the porous silica by magnesiothermic reduction. Here, two types of ordered mesoporous silica films were synthesized through EISA using two different diblock copolymers, namely, PB-PEO [poly(butadiene)-*b*-poly(ethylene oxide)] and PEP-PEO [poly-(ethylene-propylene)-*b*-poly-(ethylene oxide)]. Poly(butadiene(1,2 addition))-*b*poly(ethylene oxide), with a mass ratio of PB(5500)-*b*-PEO(5000), a block ratio of PB₁₀₂-*b*-PEO₁₁₄, and with a polydispersity index (PDI) = 1.05, was purchased from Polymer Source, Inc. Poly(ethylene-*alt*-propylene)-*b*-poly(ethylene oxide), with a mass ratio of PEP(3900)-*b*-PEO(4000), a block ratio of PEP₅₆-*b*-PEO₉₁, and with a PDI = 1.05, was synthesized using reported methods [160, 161]. Briefly, polyisoprene was grown by anionic polymerization, terminated with an -OH group and then hydrogenated over Pd/C. The resulting PEP-OH was subsequently extended by anionic polymerization of ethylene oxide.

In the synthesis of the mesoporous silica, 30 mg of diblock copolymer was dissolved in 2 mL of ethanol and 600 mg of TEOS and 300 mg of 0.01M HCl were mixed with 2 mL of ethanol in separate containers. These solutions were then mixed and the resulting solution was stirred for 1 hour and aged for 1 day. The films were dip-coated onto silicon substrates using 5-10 cm/min withdrawal rate in a chamber with 30% relative humidity. Films were dried overnight, heated at 60°C for 24 hours, and then calcined at 450°C using a 1°C/min

heat ramp in air. The mesoporous silica films produced in this way had spheroidal pores 15 nm in diameter and interpore distance of ~25 nm. To reduce silica into silicon, the mesoporous silica films were placed into a stainless steel chamber (inner volume= 5 cm³) and 5 mg of Mg was located ~1 cm away from the film. The chamber was then sealed in a glove box with an argon atmosphere. The Mg vapor was generated by heating the chamber to 675 °C using 2 hours, followed by a 5 hour soak at 675 °C. Cooled films were immersed in 1M HCl for 10 minutes to remove the magnesia. This was followed by a 10 minutes immersion in 0.5% HF to remove any residual silica. All chemistry performed on the silicon films was done under inert atmosphere.

5.2.2 Characterization

Detailed characterization for each ordered mesoporous silicon film was performed using X-ray diffraction (XRD), 2-D small angle X-ray scattering (2D-SAXS), and scanning electron microscopy (SEM). Figure 5.1 shows low angle XRD measurements for (a) PEP-PEO templated and (b) PB-PEO templated films at different stages of the synthesis process. It is evident that the mesostructure was preserved upon magnesium reduction, and after both HCl and HF washes. However, some contraction was observed due to the thermal processing. The diffraction peaks are somewhat narrower for the PEP-PEO derived material, indicative of a more periodic nanometer scale architecture, but overall, both the PEP-PEO and PB-PEO copolymers resulted in relatively well ordered cubic pore structure in the final nanoporous silicon.

Moreover, Figure 5.2 shows the 2D-SAXS patterns of a PEP-PEO templated SiO_2 film before [Figure 5.2(a)] and after [Figure 5.2(b)] Mg treatment. For small angles of incidence between the X-ray beam and the plane of substrate, the films produced patterns with distinct maxima, which can be indexed in terms of a face-centered-cubic system with (111) orientation relative to the plane of the substrate. It is evident that after Mg treatment and removal of unreacted silica, the film had retained the mesoscale order and had undergone some restructuring. The scattering patterns further indicate unidirectional lattice contraction



Figure 5.1: One-dimensional low angle X-ray diffraction patterns for (a) PEP-PEO templated and (b) PB-PEO templated films including A. mesoporous silica film before magnesium reduction (calcined at 450°C in air), B. mesoporous silicon film after Mg reduction treatment, and C. mesoporous silicon film after Mg reduction and HCl and HF washes.

perpendicular to the plane of the substrate.

Figure 5.3(a) shows an SEM image of the PEP-PEO templated silica film after calcina-



Figure 5.2: Two-dimensional small angle X-ray scattering of (a) PEP-PEO templated silica film before magnesium reduction (calcined at 450°C in air) and (b) reduced silicon film after HCl and HF washes to remove magnesia and residual silica.

tion to remove the diblock copolymer template, but before magnesium treatment. The high quality spherical pore lattice is characteristic of simple oxide phases templated with these types of large diblock copolymer. Figures 5.3(b) and 5.3(c) show top view images of mesoporous silicon films synthesized using PB-PEO and PEP-PEO, respectively, after reduction by magnesium and the subsequent HCl and HF washes. The images indicate that the PB-PEO and PEP-PEO templated silicon films have similar crystalline grain size. In addition, although the pores in the mesoporous silicon films shown in Figures 5.3(b) and 5.3(c) were not as well ordered or as regularly shaped as the pores shown in Figure 5.3(a), they retained the basic shape enforced by the template in the original silica framework. Overall, SEM images illustrate that the periodicity produced by the diblock copolymer templates is preserved in the final material.

The film thickness was measured using cross-section SEM images with ± 15 nm uncertainty. Based on the top surface SEM images, the pore size, wall thickness, and crystal size were estimated to be about 16-18 nm, 13-15 nm, and 13 nm, respectively. The porosity



Figure 5.3: Top surface SEM micrographs of (a) a PEP-PEO templated mesoporous silica film, (b) a PB-PEO templated silicon film after magnesium treatment and HCl and HF washes, and (c) a PEP-PEO templated silicon film after magnesium treatment and HCl and HF washes.

of $30\%\pm5\%$ was expected to be similar to that measured in our previous study of KLE templated mesoporous silica [69]. The $\pm5\%$ uncertainty accounted for the small change in porosity of the present samples due to the different copolymer templates and the crystalliza-

tion of silicon during the reduction process. Table 5.1 summarizes the copolymer template, porosity, film thickness, wall thickness, crystal size, and pore diameter of the mesoporous silicon films investigated.

5.2.3 Thermal Conductivity Measurement

The cross-plane thermal conductivity of ordered mesoporous silicon thin films was measured using the 3ω method with the so-called common-mode-subtraction technique [9, 76]. The principles, experimental apparatus, experimental procedure, and validation of the method have already been described in Chapter 3. The total experimental uncertainty was typically between 6% and 15% for the films investigated, and was mainly attributed to the uncertainty in the third harmonic voltage drop $V_{3\omega}$ ($\pm 2\%$) and in the film thickness t_f (± 15 nm).

5.3 Modeling

In the present study, the effective medium approximation was combined with the kinetic theory model or the minimum thermal conductivity model described previously to predict the thermal conductivity of mesoporous silicon thin films.

First, the thermal conductivity of mesoporous silicon films was predicted using the kinetic theory model given by Equation (5.7) where k_m was estimated using Equations (5.1) to (5.6). The coefficients in the relaxation time models of Equation (5.4) for Umklapp scattering $\tau_{U,i}$, defect scattering $\tau_{D,i}$, and boundary scattering $\tau_{B,i}$ were determined as $B = 1.25 \times 10^{-19}$ s/K, C = 157.2 K, $D = 3.21 \times 10^{-45}$ s³, and E = 0.0084 m by fitting Equations (5.1) to (5.4) to the thermal conductivity of high purity single crystal silicon from 10 to 1400 K reported in Ref. [14]. In mesoporous silicon, phonon scattering by film boundaries was negligible compared with phonon scattering by grain boundaries since the thickness of the films investigated was at least 10 times larger than the crystallite grain size (Table 5.1). Thus, the total relaxation time for these films was given by Equation (5.5) where the relaxation time model for phonon-grain boundary scattering $\tau_{grain,i}$ was predicted by Equation (5.6) [15]. The transmission parameter α was determined by fitting Equations (5.1) to (5.7) to the thermal conductivity of mesoporous silicon films measured between 25 and 315 K. It was found to be 0.093 and 0.051 for PEP-PEO and PB-PEO templated mesoporous silicon thin films, respectively. Both values were about 10 times smaller than those for dense (nonporous) nanocrystalline silicon reported by Wang *et al.* [15]. In fact, strong phonon scattering took place in mesoporous silicon at both inter-grain and grain-pore boundaries [15, 159]. In the latter case, no phonon could transmit into the pores, i.e., $\alpha = 0$. Overall, the averaged parameter α retrieved was greatly reduced compared with dense nanocrystalline silicon including those with high-energy grain boundaries [162].

Finally, the minimum effective thermal conductivity of mesoporous silicon can be predicted by combining Equations (5.7) and (5.8) to yield,

$$k_{eff,min} = k_{m,min} \Psi_{cp}(f_v) = k_{m,min} (1 - 1.5 f_v), \qquad (5.9)$$

where $k_{m,min}$ is the thermal conductivity of the strongly disordered matrix given by Equation (5.8). The term $(1 - 1.5f_v)$ accounts for the reduction in thermal conductivity due to the film mesoporosity.

5.4 Results and Discussion

5.4.1 Dense Nanocrystalline Silicon

Figure 5.4 shows the thermal conductivity of the dense nanocrystalline silicon film with grain size of 76 nm as a function of temperature reported by Wang *et al.* [15]. It also shows the experimental data for high purity single crystal silicon reported in Ref. [14]. The solid and dashed lines correspond to predictions from the kinetic theory model [Equations (5.1) to (5.6)] for single crystal and nanocrystalline silicon, respectively. It is evident that the thermal conductivity of the dense nanocrystalline silicon film was between 1 and 4 orders of magnitude smaller than that of single crystal silicon, depending on the temperature range examined. This can be attributed to strong phonon scattering by grain boundaries. Importantly, the model predictions agreed very well with experimental data for both single crystal silicon and dense nanocrystalline silicon, validating both of these models.



Figure 5.4: Thermal conductivity reported in the literature for high purity single crystal silicon [14] and dense nanocrystalline silicon [15] as a function of temperature. The solid and dashed lines correspond to the model predictions from the kinetic theory model [Equations (5.1) to (5.6)] for single crystal and nanocrystalline silicon, respectively.

Moreover, Figure 5.4 shows that the thermal conductivity of bulk single crystal silicon decreases with increasing temperature for temperatures above 30 K. This is due to phonon Umklapp scattering which dominated phonon scattering beyond 30 K [4]. On the other hand, the thermal conductivity of dense nanocrystalline silicon did not reach a maximum until about 200 K, after which it started to decrease with increasing temperature. This can be explained by the fact that phonon scattering by crystallite grain boundaries dominated at low temperatures while Umklapp scattering became important beyond 200 K. The measured

thermal conductivity and the model predictions for the nanocrystalline silicon were found to be proportional to T^2 at low temperatures (T < 50 K). This is also in good agreement with data reported by Wang *et al.* [15]. Note that the temperature dependence of $k \propto T^2$ is characteristic of amorphous or strongly disordered materials at low temperatures [4]. For single crystalline silicon, k is proportional to T^3 below 10 K [14].

5.4.2 Mesoporous Nanocrystalline Silicon

Table 5.2 summarizes the thermal conductivity of PEO-PEO and PB-PEO templated mesoporous nanocrystalline silicon thin films measured at different temperatures. Figure 5.5 shows the measured thermal conductivity of all PB-PEO and PEP-PEO templated ordered mesoporous nanocrystalline silicon thin films as a function of temperature. It also shows the predictions from coherent potential approximation combined with the kinetic theory model [Equations (5.1) to (5.7)] or the minimum effective thermal conductivity model [Equation (5.9)]. Figure 5.5 establishes that the measured thermal conductivity of mesoporous silicon thin films varied from 0.01 to 0.4 W/m·K as temperature increased from 25 to 315 K. The thermal conductivity was between 3 and 5 orders of magnitude smaller than that of single crystal silicon over the same temperature range. The reduction was mainly attributed to the presence of pores and strong phonon scattering by crystallite grain boundaries. Interestingly, the measured thermal conductivity of these mesoporous silicon films was about 100 times less than that reported for dense nanocrystalline silicon by Wang et al. [15]. This was due to the facts that (i) the crystallite size (13 nm) was smaller and (ii) the silicon films measured in the present study were mesoporous with porosity of about 30%. Moreover, it is interesting to note that the room temperature thermal conductivity of mesoporous silicon films ranged from 0.23 to 0.37 W/m·K. It was as low as that of mesoporous amorphous silica films [69] despite the crystallinity of the mesoporous Si films.

Comparison between PEP-PEO and PB-PEO templated films indicated that the thermal conductivity of the PB-PEO templated mesoporous silicon thin films was about 30-40% smaller than that of the PEP-PEO templated films over the entire temperature range. This



Figure 5.5: Measured thermal conductivity of mesoporous silicon thin films as a function of temperature from 25 to 315 K. The lines correspond to the model predictions from the kinetic theory model [Equations (5.1) to (5.7)] and the effective minimum thermal conductivity model [Equations (5.8) and (5.9)].

can be attributed to the fact that the PB-PEO templated films had smaller pore diameter than the PEP-PEO templated films (Table 5.1). For a given porosity, smaller pore resulted in larger pore surface area per unit volume which increased phonon scattering by pore boundaries [159]. The increased disorder in the PB-PEO templated films may also have contributed to the reduced thermal conductivity.

The differences in thermal conductivity between the PEP-PEO and PB-PEO templated films were interesting, because the films were generally very similar and differed only in the details of the nanometer scale morphology. That morphology stemmed from the structure of the initial mesoporous silica films. It can be tuned over a fairly broad range using different polymer templates and/or concentrations [69]. This results in tunable porosity, pore size, pore arrangement, and wall thickness. Because the structure of the mesoporous silica films is mostly retained during magnesium reduction, this synthetic method gives one the ability to tune the structure of the templated mesoporous nanocrystalline silicon thin films in order to achieve the desired thermal conductivity.

Moreover, examination of films of different thickness indicates that the film thickness had a negligible effects on the measured thermal conductivity for both PEP-PEO and PB-PEO templated thin films, considering the experimental uncertainty. Instead, phonon scattering by crystallite grain boundaries dominated over phonon scattering by film boundaries. The slight difference in thermal conductivity for each type of mesoporous silicon thin films could be attributed to small variations in morphology from one sample to another, including porosity, crystallite size, and wall thickness.

Figure 5.5 also establishes that the thermal conductivity predictions from the kinetic theory model, with fitting parameter $\alpha = 0.093$ for PEP-PEO templated films and $\alpha =$ 0.051 for PB-PEO templated films, captured the behavior of the measured data over the entire temperature range. In addition, the thermal conductivity of mesoporous silicon films increased monotonically with increasing temperature and reached a plateau beyond 300 K. This could be explained by the facts that (i) more phonon modes were excited as temperature increased and contributed to heat transfer and (ii) their contribution was compensated by the simultaneous increase in the phonon Umklapp scattering rate beyond 300 K. Moreover, at low temperatures (T < 50 K), both measured data and model predictions were found to be proportional to T^2 , in accordance with that observed for dense nanocrystalline silicon [15]. Indeed, mesoporous nanocrystalline silicon has a strongly disordered nanostructure, similar to the dense nanocrystalline silicon and thus, it features amorphous-like thermal conductivity at low temperatures.

Finally, it is interesting to note that the predictions from the minimum effective thermal conductivity model [Equation (5.9)] also varied linearly with T^2 at low temperatures. However, this model failed to predict the temperature dependence of the measured data at high temperatures. This can be attributed to the fact that, at high temperatures, numerous phonon modes contributed to heat transfer and Umklapp scattering became important resulting in more crystalline-like thermal conductivity which was not captured by the minimum thermal conductivity model.

5.5 Conclusions

This chapter reported preparation, characterization, and cross-plane thermal conductivity measurements for ordered mesoporous nanocrystalline silicon thin films from 25 to 315 K. Overall, the measured thermal conductivity was between 3 and 5 orders of magnitude smaller than that of bulk single crystal silicon, depending on the temperature range examined. In addition, thin films templated by PB-PEO copolymer had smaller thermal conductivity than those templated by PEP-PEO copolymer due to their smaller pores and increased disorder. The mesoporous silicon thin films had amorphous-like thermal conductivity proportional to T^2 at low temperatures. On the other hand, they had crystalline-like thermal conductivity at high temperatures as it reached a maximum and plateau beyond 300 K. Finally, a kinetic theory model was used to predict the effective thermal conductivity of mesoporous silicon thin films accounting for (i) phonon scattering by defects and crystallite grain boundaries as well as due to Umklapp scattering in the nanocrystalline matrix and (ii) the porosity of the films. Good agreement was found between the measured data and the model predictions. These results and the model could help establish new strategies to control the thermal conductivity of mesoporous silicon for a wide range of applications including thermoelectric energy conversion.

Sample No.	Template	Porosity	Thickness	Wall thickness	Crystal size	Pore diameter
#		f_v (%)	t_f (nm)	t_w (nm)	$d_{cryst} \; (\mathbf{nm})$	d_p (mm)
1	PEP-PEO	30 ± 5	$140{\pm}15$	13-15	$\sim \! 13$	$\sim \! 18$
2	PEP-PEO	30 ± 5	175 ± 15	13-15	$\sim \! 13$	$\sim \! 18$
ŝ	PEP-PEO	30 ± 5	$260{\pm}15$	13-15	$\sim \! 13$	$\sim \! 18$
4	PB-PEO	30 ± 5	$148{\pm}15$	13-15	$\sim \! 13$	~ 16
ю	PB-PEO	30 ± 5	$235{\pm}15$	13-15	$\sim \! 13$	~ 16
9	PB-PEO	30 ± 5	$340{\pm}15$	13-15	$\sim \! 13$	~ 16

B D	1					
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Т	PEP-PEO templated samples			PB-PEO templated samples		
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(K)	Sample 1	Sample 1 Sample 2		Sample 4	Sample 5	Sample 6
25	$0.022 {\pm} 0.002$	$0.027 {\pm} 0.002$	$0.028 {\pm} 0.002$	$0.018 {\pm} 0.002$	$0.014{\pm}0.001$	$0.017 {\pm} 0.001$
30	$0.033 {\pm} 0.004$	$0.040 {\pm} 0.004$	$0.042 {\pm} 0.003$	$0.025 {\pm} 0.003$	$0.021 {\pm} 0.001$	$0.024{\pm}0.001$
36.5	$0.049 {\pm} 0.006$	$0.056 {\pm} 0.005$	$0.061 {\pm} 0.003$	$0.038 {\pm} 0.004$	$0.030 {\pm} 0.002$	$0.033 {\pm} 0.002$
44.5	$0.070 {\pm} 0.008$	$0.076 {\pm} 0.007$	$0.083 {\pm} 0.005$	$0.050 {\pm} 0.005$	$0.041 {\pm} 0.003$	$0.045 {\pm} 0.002$
54.2	$0.093 {\pm} 0.010$	$0.098 {\pm} 0.009$	$0.11 {\pm} 0.01$	$0.066 {\pm} 0.007$	$0.054{\pm}0.004$	$0.059 {\pm} 0.003$
66	$0.12{\pm}0.01$	$0.12{\pm}0.01$	$0.14{\pm}0.01$	$0.084{\pm}0.009$	$0.070 {\pm} 0.005$	$0.074{\pm}0.004$
80.4	$0.15 {\pm} 0.02$	$0.15 {\pm} 0.01$	$0.17 {\pm} 0.01$	$0.11 {\pm} 0.01$	$0.088 {\pm} 0.006$	$0.094{\pm}0.005$
98	$0.18 {\pm} 0.02$	$0.18 {\pm} 0.02$	$0.20 {\pm} 0.01$	$0.13{\pm}0.01$	$0.11 {\pm} 0.01$	$0.12{\pm}0.01$
119.3	$0.21 {\pm} 0.02$	$0.22 {\pm} 0.02$	$0.24{\pm}0.02$	$0.16{\pm}0.02$	$0.13 {\pm} 0.01$	$0.14{\pm}0.01$
145.4	$0.25 {\pm} 0.03$	$0.25{\pm}0.02$	$0.28 {\pm} 0.02$	$0.18{\pm}0.02$	$0.15 {\pm} 0.01$	$0.16{\pm}0.01$
177.1	$0.27 {\pm} 0.03$	$0.28 {\pm} 0.03$	$0.31{\pm}0.02$	$0.21 {\pm} 0.02$	$0.18 {\pm} 0.01$	$0.19{\pm}0.01$
215.7	$0.31 {\pm} 0.04$	$0.31 {\pm} 0.03$	$0.34{\pm}0.02$	$0.23 {\pm} 0.03$	$0.20{\pm}0.01$	$0.21{\pm}0.01$
262.7	$0.33 {\pm} 0.04$	$0.34{\pm}0.03$	$0.37 {\pm} 0.03$	$0.25 {\pm} 0.03$	$0.22{\pm}0.02$	$0.23{\pm}0.01$
293	$0.32{\pm}0.04$	$0.34{\pm}0.03$	$0.37 {\pm} 0.03$	$0.26{\pm}0.03$	$0.23 {\pm} 0.02$	$0.25{\pm}0.01$
315	$0.32{\pm}0.04$	$0.35{\pm}0.03$	$0.37 {\pm} 0.03$	$0.25{\pm}0.03$	$0.23 {\pm} 0.02$	$0.25 {\pm} 0.01$

 Table 5.2: Measured thermal conductivity (in W/m·K) of PEO-PEO and PB-PEO templated

 ordered mesoporous nanocrystalline silicon thin films.

Nomenclature

a_i, b_i, c_i, d_i	Constants in a fourth order polynomial dispersion relation
В	Fitting parameter in Umklapp scattering relaxation time model $[\mathrm{s}/\mathrm{K}]$
C	Fitting parameter in Umklapp scattering relaxation time model [K]
d_{cryst}	Crystallite grain size [m]
d_p	Pore diameter [m]
D	Fitting parameter in defect scattering relaxation time model $[s^3]$
E	Fitting parameter in boundary scattering relaxation time model [m]
f_{BE}	Bose-Einstein distribution
f_v	Porosity
k	Thermal conductivity $[W/m \cdot K]$
k_B	Boltzmann constant $[1.38\times 10^{-23}~{\rm J/K}]$
K	Wavenumber $[m^{-1}]$
n	Number of atoms per unit volume of material $[m^{-3}]$
v_g	Group velocity [m/s]

Symbols

α	Fitting parameter accounting for phonon transmission [-]
$ heta_i$	Characteristic temperature in the Cahill-Pohl thermal conductivity model [K]
τ	Phonon relaxation time [s]
ω	Frequency [rad/s]
\hbar	Reduced Planck's constant $[1.054\times 10^{-34}~{\rm m^2\cdot kg/s}]$
\mathcal{D}	Phonon density of states
Ψ	Effective medium approximation

Subscripts

bulk	Refers to bulk dense crystalline silicon
В	Refers to phonon-boundary scattering
cp	Refers to the coherent potential effective medium approximation

cryst	Refers to crystallite
D	Refers to phonon-defect scattering
eff	Refers to effective properties
f	Refers to thin film
grain	Refers to crystallite grain boundary
i	Refers to transverse or longitudinal polarization
m	Refers to dense matrix material
max	Refers to cut-off frequency or wavenumber
min	Refers to the Cahill-Pohl minimum thermal conductivity model
NC	Refers to nanocrystalline silicon
U	Refers to phonon Umklapp scattering

CHAPTER 6

Scaling Laws for Thermal Conductivity of Crystalline Nanoporous Silicon

As discussed in Chapter 5, a physical model combining kinetic theory and effective medium approximation can capture the measured thermal conductivity of ordered mesoporous nanocrystalline silicon. However, this model contains several empirical parameters and requires data fitting. In addition, the ranges of the samples' porosity and pore size are relatively narrow. Molecular dynamics simulations represent an interesting alternative to both experiments and physical modeling as discussed in Chapter 2. This chapter presents a combination of nonequilibrium molecular dynamics simulations and physical modeling to investigate the effects of the (i) system length, (ii) pore diameter, and (iii) porosity, on the thermal conductivity of ordered nanoporous crystalline silicon.

6.1 Introduction

6.1.1 Molecular Dynamics Simulations

Molecular dynamics (MD) simulations solve the Newton's equation of motion of individual atoms whose interactions are governed by an empirical interatomic potential. Two main approaches have been developed to predict thermal conductivity using MD simulations, namely (i) the equilibrium Green-Kubo approach and (ii) the direct non-equilibrium molecular dynamics (NEMD) approach [163]. These two approaches have been described in detail in the literature [16,99,101–103,163]. MD simulations are increasingly used to investigate physical phenomena controlling energy transport in both bulk dense and nanostructured materials. In particular, Lee *et al.* [19] investigated the transverse thermal conductivity of nanoporous silicon with periodically arranged cylindrical pores at 300 K using MD simulations. The authors performed equilibrium MD simulations using the Einstein relation [164] similar to the Green-Kubo relation [101, 102]. Note that the simulation cell contained only one cylindrical pore and the atoms at the surface of the pore were passivated with hydrogen atoms. The thermal conductivity predicted by this equilibrium method corresponds to the bulk property. The porosity and pore diameter ranged from 7% to 38% and from 0.63 to 2.26 nm, respectively. The Tersoff type potential was used to model interatomic Si-Si and Si-H interactions [165]. This potential overestimated the thermal conductivity of dense crystalline Si by about 80% compared with experimental measurements at 300 K [19]. The authors indicated that the predicted thermal conductivity of nanoporous Si at 300 K was more than two orders of magnitude smaller than that of dense crystalline silicon [19]. They also showed that the thermal conductivity of porous silicon (i) decreased with increasing pore diameter for a given pore spacing, and (ii) increased with increasing pore spacing for a given pore diameter [19].

Moreover, the non-equilibrium molecular dynamics (NEMD) simulations can predict the thermal conductivity from the temperature gradient and heat flux flowing through a simulation system. It is ideal for investigating finite size effect for structures such as thin films and superlattices [16,163]. This method had previously been implemented to predict the thermal conductivity of dense solid materials such as silicon [16], quartz [106], dense and nanoporous amorphous silica [92, 105, 109]. Recently, Lee *et al.* [20] investigated the effect of randomly dispersed vacancy defects on the thermal conductivity of crystalline silicon using NEMD simulations with the Tersoff potential. The authors considered tetrahedral, hexahedral, and dodecahedral-like vacancy clusters with vacancy concentration (i.e., porosity) ranging from 0.15% to 1.5% [20]. Considering the induced strain fields, their effective diameters were estimated as 1.33, 1.50, and 1.70 nm, respectively. Note that each vacancy cluster contained only 4 to 12 atoms and the maximum vacancy concentration simulated did not exceed 1.5%. The thermal conductivity at 300 K was found to decrease by 95% with porosity of 1.5%. It was not affected by the size of the clusters above the vacancy concentration of 1% [20].

6.1.2 Physical Modeling

The thermal conductivity of nanoporous crystalline materials was reported to depend on both the porosity and the pore size [19, 57, 152, 166, 167]. Alvarez *et al.* [167] studied the influence of porosity and pore size on the thermal conductivity of crystalline porous silicon using the phonon hydrodynamics approach. The authors considered monodisperse spherical pores randomly dispersed in a three-dimensional crystalline silicon matrix. They expressed the effective thermal conductivity as [167],

$$k_{eff} = k_m \frac{1}{\frac{1}{f(f_v)} + 18f_v \frac{(l/d_p)^2}{1 + 2A'(l/d_p)} \left(1 + \frac{3}{\sqrt{2}}\sqrt{f_v}\right)},$$
(6.1)

where k_m is the thermal conductivity of dense matrix material, f_v is the porosity, d_p is the pore diameter, l is the dominant phonon mean free path (MFP) in bulk dense silicon, $f(f_v) = (1-f_v)^3$ based on percolation theory [168,169], and A' is a function of l/d_p expressed by Millikan [170] as $A' = 0.864 + 0.29 \exp(-0.625 d_p/l)$. The authors compared predictions of Equation (6.1) with experimental results at room temperature for electrochemically etched porous silicon with porosity ranging from 40% to 90% and vertical cylindrical pores with radius ranging from 1 to 100 nm [167]. Good agreement was found by taking the dominant phonon MFP l for silicon at 300 K as 40 nm [167]. However, this value was smaller than that of about 300 nm suggested in the literature [171,172]. This latter value was derived by considering the phonon dispersion and assuming that only the acoustic phonons contributed to heat transfer [171,172].

As previously discussed, Lee *et al.* [19] investigated the transverse thermal conductivity of nanoporous silicon with cylindrical pores at room temperature using MD simulations. The authors also correlated their results with the ballistic-diffusive model developed by Prasher [166] for two-dimensional systems and expressed as [166],

$$k_{eff} = k_m \frac{1}{\frac{1}{f(f_v)} + \alpha \frac{\sqrt{f_v}}{F(f_v)} \frac{1}{d_p}},$$
(6.2)

where $F(f_v) = \sqrt{4f_v/\pi} (\sin^{-1}\sqrt{4f_v/\pi} - \pi/2) + \sqrt{1 - 4f_v/\pi}$ and $f(f_v) = (1 - f_v)(1 + \beta f_v^{\gamma})$.

The three empirical fitting parameters α , β , and γ were fitted against MD simulation results for k_{eff} as $\alpha = 50.9$, $\beta = 1821.1$, and $\gamma = 1.9$, respectively [19].

The present study aims to predict the thermal conductivity of crystalline nanoporous silicon using NEMD simulations. Multiple spherical pores organized in a simple cubic lattice were introduced into a crystalline silicon matrix. First, the simulation procedure was validated with results for dense crystalline silicon reported in the literature [16–18]. Then, the thermal conductivity of nanoporous crystalline silicon was computed at 500 K for various system morphology including porosity, pore diameter, and system length. Finally, a physics-based model predicting the effects of these parameters on the thermal conductivity of nanoporous silicon was developed.

6.2 Analysis

6.2.1 Thermal Conductivity Prediction using NEMD Simulations

The detailed procedure of the NEMD simulations used in the present study has already been described by Coquil *et al.* [92] and need not be repeated. In brief, the thermal conductivity was estimated using the so-called Müller-Plathe method [103, 109]. It consists of imposing a heat flux q''_z along the z-direction and determining the resulting temperature gradient dT_{MD}/dz to estimate the thermal conductivity as [16],

$$k = -\frac{q_z''}{\mathrm{d}T_{MD}/\mathrm{d}z}.\tag{6.3}$$

The heat flux was imposed by a velocity swapping technique described in the literature [103, 109]. To do so, the atoms with the largest kinetic energy (i.e., the hottest) in the heat sink were exchanged with those with the lowest kinetic energy (i.e., the coolest) in the heat source. The simulation cell was first divided into an even number of slices. The temperature of each slice and its gradient were calculated by averaging the atomic kinetic energy over time as well as over all the atoms in the slice. The temperature $T_{MD}(z)$ of a slice along the z-direction (i.e., the direction of the heat flux) at every time step was determined from the

classical statistical mechanics equipartition theorem as [109],

$$T_{MD}(z) = \frac{1}{3n_k k_B} \sum_{i=1}^{n_k} m_i v_i^2, \qquad (6.4)$$

where $k_B = 1.38 \times 10^{-23} \text{ m}^2 \text{kg/s}^2 \text{K}$ is the Boltzmann's constant, n_k is the number of atoms in the slice about z, and m_i and v_i are the mass and velocity of individual atoms *i*, respectively. The temperature of each slice was then averaged over multiple time steps. The number of atoms per slice n_k was chosen to be larger than 32 following Schelling *et al.* [16]. After reaching steady state, a temperature profile $T_{MD}(z)$ decreasing from the center to the ends of the simulation cell could be estimated using Equation (6.4). A total number of 6 to 8 million steps were simulated for a microcanonical or NVE ensemble, in which the total number of atoms, total volume, and total energy of the system were conserved. In addition, periodic boundary conditions were imposed in all directions. Finally, the thermal conductivity was retrieved using Equation (6.3) by averaging over the last 2 million time steps. The numerical procedure was implemented using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [173]. Simulations were run in parallel on 32 to 128 64-bit nodes with 1024 to 2048 MB of RAM.

It should be noted that the expression for temperature $T_{MD}(z)$ given by Equation (6.4) is widely used in MD simulations. However, T_{MD} represents the real temperature T only if the latter is much larger than the Debye temperature T_{Debye} [174]. In cases when the system temperature is lower than T_{Debye} , T_{MD} needs to be corrected for quantum effects [174]. For silicon, $T_{Debye} = 650$ K [16] and according to Volz and Chen [174] and Tang [175], quantum corrections are negligible when T_{MD} exceeds 500 K for crystalline silicon systems.

6.2.2 Validation

MD simulations were first validated with dense crystalline silicon. The well established two- and three-body interactions Stillinger and Weber (SW) potential [176] was used. It is known to successfully describe the elastic constants and thermal expansion coefficients, as well as phonon dispersion relations of dense silicon [177–179]. It was also previously used to model silicon thermal conductivity above 500 K [16]. Here, simulation systems consisted of six silicon unit cells in both the x- and y-directions, with each unit cell consisting of a diamond cubic arrangement of eight silicon atoms. The lattice constant a of each unit cell was 5.43 Å. On the other hand, the number of unit cells along the z-direction varied from 48 to 384. Results for thermal conductivity were analyzed as a function of the simulation system length L_z ranging from 26 to 104 nm. The total number of atoms varied from 13,824 to 55,294. Simulations were performed at both 500 and 1,000 K. The simulation time step was set to be 0.55 fs and simulations were run for a total of 6 million time steps. This corresponded to an effective time of 3.3 ns which was more than twice as long as the total time used by Schelling *et al.* [16] and well above the 1 ns limit necessary to reach a steady-state temperature profile [16]. The equations of motion were integrated using a velocity Verlet algorithm [99]. The rate of velocity exchanges was chosen so that the corresponding heat flux was approximately $1.8 \times 10^{11} \text{ eV/nm}^2 \cdot \text{s}$, in agreement with that used by Schelling *et al.* [16]. The simulation systems were divided into slices corresponding to 1/4 of a silicon unit cell. Note that the temperature profile was found to have already converged after the first 2 million steps.

The temperature profile was linear except for the slices within the heat source and heat sink regions, both corresponding to about 20% of the simulation system length. The nonlinearity in temperature observed around those regions was attributed to the strong scattering caused by the heat source and sink [180]. The linear part of the temperature profile was fitted with a linear function, $T_{MD}(z)$, and the resulting gradient, dT_{MD}/dz , was used in Equation (6.3) to estimate the thermal conductivity. The gradients estimated for the two different linear regions, on each side of the heat source, typically differed by less than 10%. This difference was used to estimate the error associated with the retrieved thermal conductivity. Note that the system length L_z represents half of the total length of the simulation cell along the z-direction.

Figure 6.1 plots 1/k as a function of $1/L_z$ at 500 and 1,000 K along with results previously reported by Schelling *et al.* [16] and bulk properties for natural and isotopically enriched silicon reported in the literature [17, 18]. It establishes that results obtained in the present study were in excellent agreement with those previously reported by Schelling *et al.* [16]. In addition, the bulk thermal conductivity can be estimated by extrapolating the linear fit (solid lines) for 1/k vs. $1/L_z$ as $1/L_z$ tends to zero or L_z tends to infinity [16]. Then, the thermal conductivity of bulk silicon was found to be 141 ± 25 W/m·K at 500 K and 46 ± 2 W/m·K at 1,000 K. The measured thermal conductivity of natural Si at 500 and 1,000 K were about 80 and 30 W/m·K, respectively [17]. That of isotopically enriched Si, known to contain fewer defects than natural Si, was estimated to be 120 W/m·K at 500 K [16, 18]. This was in reasonable agreement with the present MD simulations results.



Figure 6.1: Predicted values of 1/k as a function of $1/L_z$ for crystalline silicon at 500 and 1000 K along with similar results reported by Schelling *et al.* [16]. Experimental data for bulk natural silicon [17] and isotopically enriched pure silicon [18] are also displayed.

6.2.3 Thermal Conductivity of Nanoporous Silicon

In order to simulate crystalline nanoporous silicon, simulation cells of crystalline silicon were first generated. Here, the simulation cells had the same size (6 to 12 unit cells) along both the x- and y-directions and had 48 to 480 unit cells along the z-direction. Then, spherical pores, in a simple cubic arrangement, were introduced by removing silicon atoms within a spherical region along the centerline of the crystalline lattice. Figure 6.2 shows the 2D atomic structures of a typical crystalline nanoporous silicon phase with two pores, 2.6 nm in diameter, inserted in a $3.26 \times 3.26 \times 6.52$ nm³ simulation cell. The structure represented a cross-section in the y-z plane which intercepted the center of pores. Note that, in the present study, there was no passivation on the pore surface, i.e., silicon atoms on the pore surface have dangling bonds.



Figure 6.2: Typical atomic structures of the nanoporous crystalline silicon phase with two spherical pores of 2.6 nm in diameter aligned along the z-direction of a $3.26 \times 3.26 \times 6.52$ nm³ simulation cell. This 2D representation corresponds to the projection of 1 nm thick slab in the out-of-plane direction.

Here also, the time step was 0.55 fs. Initially, the system temperature was uniform and set to be 515 ± 15 K by imposing constant number of atoms, volume and temperature (NVT ensemble) for 20,000 time steps. Then, the system was set to equilibrium under constant number of atoms, volume and energy (NVE ensemble) condition for another 20,000 time steps. Finally, the simulation was performed in the NVE ensemble for 6 to 8 million time steps with velocity exchange rate adjusted to impose a heat flux of approximately 1.8×10^{11} $eV/nm^2 \cdot s$ (i.e., $2.9 \times 10^{10} \text{ W/m}^2$). Note that the pore shape remained spherical throughout the simulations. The z-direction of the simulation cell was divided into slices corresponding to 1/2 of a silicon unit cell and containing more than 50 atoms. The procedure used to estimate the temperature gradient and to calculate the thermal conductivity was identical to that previously described for dense silicon. The temperature profile was found to have already converged after the first 4 million steps.

Finally, Table 6.1 summarizes the values of porosity f_v , spherical pore diameter d_p , crosssectional area A_c , system length L_z , and pore number N of the crystalline nanoporous silicon systems investigated in the present study. The porosity ranged from 8% to 38% while pore diameter varied from 1.74 to 5.86 nm. The system length was between 13 and 130 nm corresponding to 4 to 32 aligned pores.

6.3 Result and Discussion

6.3.1 Effects of System Length and Pore Diameter

Figures 6.3(a) and 6.3(b) show the predicted effective thermal conductivity at 500 K of crystalline nanoporous silicon k_{eff} as a function of system length L_z for different pore diameters d_p with porosity f_v equal to 27% and 38%, respectively. They indicate that the thermal conductivity of nanoporous crystalline silicon was more than one order of magnitude smaller than that of dense crystalline silicon at 500 K (see Figure 6.1) [16–18]. This was due to the fact that the presence of the nanosize pores greatly enhances phonon scattering. Note that similar reduction in thermal conductivity was observed for only 1.5% vacancy concentration as reported by Lee *et al.* [20]. This could be attributed to the facts that vacancy defects introduced large strain fields in regions of the materials with size comparable to the pore diameter used in the present study [20]. These randomly distributed defect-induced strain fields caused large rate of phonon scattering by clusters and effectively obstruct the cross-sectional area for phonon transport [20]. In addition, Figure 6.3 also establishes that the thermal conductivity of crystalline nanoporous silicon systems for a given porosity (i) increased with increasing L_z for a given pore diameter d_p and (ii) increased with increasing pore diameter d_p for a given length L_z . Similar results and conclusions were found for the other values of porosity investigated (Table 6.1).

Moreover, it is interesting to note that Coquil *et al.* [92] established that the system length had no effect on the thermal conductivity of amorphous nanoporous SiO₂ when the system length was larger than approximately 5 nm for $d_p = 1.8$ nm and $f_v = 25 \pm 2\%$. The different behavior observed with crystalline nanoporous Si can be attributed to their crystalline nature in which phonon modes have significantly longer mean free path (MFP) than in amorphous materials.

6.3.2 Effect of Porosity

Figure 6.4 shows the thermal conductivity of nanoporous silicon at 500 K as a function of system length for porosity ranging from 8% to 38%. Here, the pore diameter d_p was maintained at 2.8±0.2 nm and the porosity of nanoporous silicon systems was adjusted by varying the cross-sectional area A_c . It is evident that the thermal conductivity decreased with increasing porosity. In addition, the system length L_z had stronger effect on thermal conductivity for systems with smaller porosity. For example, the thermal conductivity of nanoporous silicon with porosity $f_v = 8\%$ and 38% increased by 85% and 40%, respectively, as L_z increased from 22 to 109 nm. This was due to the fact that, in systems with large porosity, phonon scattering by pores dominated over phonon scattering by film boundaries.

6.3.3 Bulk Thermal Conductivity of Nanoporous Silicon

The bulk thermal conductivity of nanoporous Si can be determined by linear extrapolation of 1/k vs. $1/L_z$ as $L_z \to \infty$ [16]. Sellan *et al.* [181] indicated that the minimum system length used should be comparable to the largest MFP of the dominant phonons. The authors further defined the maximum thermal conductivity k_{max} that can be accurately predicted



Figure 6.3: Predicted effective thermal conductivity of crystalline nanoporous silicon at 500 K as a function of system length L_z for porosity (a) $f_v = 27\%$ and (b) $f_v = 38\%$ along with various pore diameters d_p and simulation cell cross-section A_c .



Figure 6.4: Predicted effective thermal conductivity of crystalline nanoporous silicon at 500 K as a function of system length for pore diameter $d_p = 2.8 \pm 0.2$ nm and porosity f_v between 8% and 38%.

using the linear extrapolation procedure with a minimum system length L_{min} as [181],

$$k_{max} = \frac{L_{min}k_B v_g}{6a^3},\tag{6.5}$$

where a is the lattice constant and v_g is the average phonon group velocity given by [181],

$$v_g = \frac{1}{3} \left(v_{g,L} + 2v_{g,T} \right), \tag{6.6}$$

where $v_{g,L}$ and $v_{g,T}$ are the longitudinal and transverse phonon group velocities, respectively. Note that the above requirement was validated against results of MD simulations for argon and dense crystalline silicon [16, 181]. Here, we further expressed the group velocities $v_{g,L}$ and $v_{g,T}$ in nanoporous crystalline Si as [182],

$$v_{g,L} = [(K_{eff} + 4G_{eff}/3)/\rho_{eff}]^{1/2}$$
 and $v_{g,T} = (G_{eff}/\rho_{eff})^{1/2}$, (6.7)

where K_{eff} , G_{eff} , and ρ_{eff} are the effective bulk modulus, shear modulus, and density of the nanoporous material, respectively [182]. For porous material of porosity f_v , the effective bulk modulus K_{eff} has been expressed as [183],

$$K_{eff} = K_m \left[1 - f_v \left(1 + \frac{3K_m}{4G_m} \right) \right], \tag{6.8}$$

where K_m and G_m are the bulk and shear modulus of the continuous dense matrix. Similarly, the effective shear modulus G_{eff} can be expressed as [183],

$$G_{eff} = G_m \left[1 - f_v \left(1 + \frac{2G_m \left(3\lambda_m + 8G_m \right)}{9G_m \lambda_m + 14G_m^2} \right) \right],$$
(6.9)

where λ_m is the Lamé's elastic constant of the dense matrix [183]. In addition, the effective density ρ_{eff} is given by $\rho_{eff} = \rho_m(1 - f_v)$. The density ρ_m , the bulk modulus K_m , the shear modulus G_m , and the Lamé's constant λ_m for the dense crystalline silicon matrix were calculated from previously reported MD simulations using the Stillinger-Weber potential as 2300 kg/m³, 71.5 GPa, 52.4 GPa, and 36.6 GPa, respectively [178]. For comparison, the experimental data for ρ_m , K_m , G_m , and λ_m were 2329 kg/m³, 59.6 GPa, 79.6 GPa, and 6.5 GPa, respectively [184]. Then, the phonon group velocities $v_{g,L}$, $v_{g,T}$, and v_g of nanoporous silicon were calculated using Equations (6.6) to (6.9). Finally, considering that the minimum system length L_{min} simulated was 50 nm, i.e., $1/L_z < 0.02 \text{ nm}^{-1}$, the maximum thermal conductivity k_{max} predicted by Equation (6.5) ranged between 3 and 5 W/m·K for systems with porosity between 8% and 38%. Note that the same conclusions were reached by using the above experimentally measured elastic properties [184].

Figures 6.5(a) and 6.5(b) show the predicted values of $1/k_{eff}$ at 500 K as a function of $1/L_z$ for crystalline nanoporous silicon with porosities of 27% and 38%, respectively. Systems satisfying $1/L_z < 0.02 \text{ nm}^{-1}$ were used for linear extrapolation. Except for systems with 8% porosity, the predicted thermal conductivity of bulk nanoporous silicon $k_{eff} (L_z \to \infty)$ was less than or equal to k_{max} , confirming the validity of the linear extrapolation of $1/k_{eff}$ vs. $1/L_z$ [181]. For systems with 8% porosity, simulations of systems significantly longer than those simulated would be required.



Figure 6.5: Predicted values of $1/k_{eff}$ of crystalline nanoporous silicon at 500 K as a function of $1/L_z$ for porosity (a) $f_v = 27\%$ and (b) $f_v = 38\%$ along with various pore diameter d_p and simulation cell cross-section A_c . Linear extrapolation used data satisfying $1/L_z < 0.02$ nm⁻¹ ($L_z > 50$ nm).

6.3.4 Physical Modeling

6.3.4.1 Effective medium approximations

The effect of porosity on various properties of porous materials is usually accounted for by some effective medium approximations (EMAs), as discussed in Chapter 2. Here, the pores in nanoporous silicon are so small that their thermal conductivity can safely be neglected as explained in Refs. [92, 93]. Then, the coherent potential model is expressed as [8, 98],

$$k_{eff} = k_m \Psi_{cp}(f_v) = k_m (1 - 1.5 f_v).$$
(6.10)

This model was first derived by Landauer [98] for the effective dielectric properties of random mixtures of spherical inclusions in a continuous matrix. Cahill and Allen [8] successfully applied the coherent potential model to predict the thermal conductivity of Vycor glass from 30 to 300 K with pore diameter and porosity approximately equal to 10 nm and 30%, respectively. More recently, this model was also found to agree well with predictions of thermal conductivity of amorphous mesoporous silica at 300 K obtained by non-equilibrium MD simulations [92].

Finally, note that the above EMAs do not directly account for the effect of pore diameter. However, Figures 6.3 and 6.5 show that d_p has significant effect on k_{eff} for a given porosity. Thus, the coherent potential model and most other EMAs, in their conventional form $k_{eff} = k_m \Psi(f_v)$, are inadequate to predict the effective thermal conductivity of crystalline nanoporous media.

6.3.4.2 Effect of interfacial area concentration

It has been established that the reduction of thermal conductivity of nanocomposite material is mainly due to phonon scattering by interfaces [19, 139, 185, 186]. The phonon-interface scattering rate is known to increase with increasing interfacial area concentration A_i (in m^{-1}) defined as the surface area of interface per unit volume of nanocomposite material [139,185,186]. In porous material with spherical pores arranged in a simple cubic lattice, the interfacial area concentration can be expressed as $A_i = 6f_v/d_p$. Thus, for a given porosity f_v , A_i increases with decreasing pore diameter d_p . Figure 6.3 suggests that k_{eff} decreased not only with increasing f_v but also with decreasing d_p and thus with increasing A_i .

Moreover, the systems simulated in the present study fell in the ballistic regime characterized by $l/d_p \gg 10$ [187]. Then, the phonon hydrodynamics model given by Equation (6.1) for spherical pores simplifies to,

$$k_{eff} = k_m \frac{1}{1.3l \left(1 + \frac{3}{\sqrt{2}}\sqrt{f_v}\right) A_i}.$$
 (6.11)

The relative difference between predictions by Equations (6.1) and (6.11) for nanoporous silicon systems investigated in the present study was less than 1%. More importantly, Equation (6.11) suggests that the thermal conductivity of nanoporous silicon is inversely proportional to A_i .

Similarly, for cylindrical pores with the same ranges of pore diameter and porosity explored in this study, the ballistic diffusive model given by Equation (6.2) simplifies to $k_{eff} = k_m \alpha \sqrt{f_v} F(f_v) / A_i$, where for periodically arranged cylindrical pores $A_i = 4f_v / d_p$. Here also, the thermal conductivity appears to be inversely proportional to A_i .

Unfortunately, predictions by Equation (6.11) underestimated the thermal conductivity computed by our MD simulations by about 90% at 500 K using $k_m = 80$ W/m·K for high purity crystalline silicon [17] and $l \simeq 140$ nm [171]. To improve the predictions of Equation (6.11), the MFP l could be treated as a fitting parameter. Alternatively, a new physics-based model was developed in the present study.

6.3.4.3 Modeling

This section presents a model for the effective thermal conductivity of mesoporous Si based on kinetic theory and able to simultaneously account for the effects of porosity, interfacial area concentration, and system length. The kinetic theory expresses the thermal conductivity k_m of the dense matrix in nanoporous materials as [85],

$$k_m = \frac{1}{3} c_{v,m} v_{g,m}^2 \tau_{eff}.$$
 (6.12)

The total relaxation time τ_{eff} includes the contributions from (i) phonon Umklapp scattering τ_U as well as phonon scattering by (ii) pores τ_P , and (iii) film boundaries τ_B . Here, Umklapp scattering rate was estimated based on the phonon MFP in bulk dense silicon as τ_U^{-1} = $v_{g,m}/l$ where $l \simeq 140$ nm [171]. The relaxation time for phonon scattering by large defect aggregates [188] was adopted to account for phonon-pore scattering. It was expressed as $\tau_P^{-1} = v_{g,m} n \pi d_p^2 / 4$, where n is the number density of pores of diameter d_p . For spherical pores, $n = 6f_v/(\pi d_p^3)$ so that the phonon-pore scattering rate can be expressed as $\tau_P^{-1} = v_{g,m}A_i/4$. This corresponds to an average phonon-pore scattering MFP of $4/A_i$ in good agreement with that derived by Minnich and Chen [185] for phonon-interface scattering in nanocomposites. In addition, phonon-boundary scattering can be expressed as $\tau_B^{-1} = v_{g,m}/L_z$ [17], where L_z corresponds to the thickness of nanoporous silicon thin films. In nanoporous materials, Umklapp scattering is typically negligible compared with phonon scattering by pores and by film boundaries, i.e., $\tau_U^{-1} \ll \tau_P^{-1}$ and $\tau_U^{-1} \ll \tau_B^{-1}$. These conditions can also be formulated in terms of pore number density or porosity as $n \gg 4/\left(l\pi d_p^2\right)$ or $f_v \gg 2d_p/\left(3l\right)$ and in terms of system length as $L_z \ll l$, respectively. In the present study, the number density of pores n was at least 10 times larger than $4/(l\pi d_p^2)$ for all systems simulated. This verified that Umklapp scattering was negligible compared with phonon scattering by pores. Then, according to Matthiessen's rule, the total relaxation time τ_{eff} can be expressed as [17],

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_P} + \frac{1}{\tau_B} = v_{g,m} \left(\frac{A_i}{4} + \frac{1}{L_z}\right).$$
(6.13)

Combining EMAs, accounting for the effect of porosity on k_{eff} , with the matrix thermal conductivity k_m , accounting for the effect of phonon-pore scattering, the effective thermal conductivity of nanoporous silicon systems can be expressed as,

$$k_{eff} = k_m \Psi(f_v) = \frac{1}{3} c_{v,m} v_{g,m} \frac{\Psi(f_v)}{A_i/4 + 1/L_z}.$$
(6.14)

It is evident that as L_z tends to infinity, the bulk effective thermal conductivity k_{eff} is inversely proportional to A_i in agreement with the phonon hydrodynamic model for spherical pores [167] and the ballistic diffusive model for cylindrical pores in the ballistic regime [166].

Furthermore, the specific heat $c_{v,m}$ and the group velocity $v_{g,m}$ of the silicon matrix may differ from those of dense bulk silicon due to band folding and phonon confinement effect [153, 189]. In fact, Hopkins *et al.* [153] recently observed, using the plane-wave expansion technique [190], a large reduction in phonon group velocity in single crystalline nanoporous silicon films made by phononic crystal patterning. The main purpose of the present study was to investigate the scaling laws predicting the effects of morphological parameters on the thermal conductivity of nanoporous silicon. To facilitate the scaling analysis and considering the approximate nature of potentials used in MD simulations, the product $c_{v,m}v_{g,m}/3$ was substituted by a semi-empirical parameter β so that the effective thermal conductivity can be written as,

$$k_{eff} = \beta \frac{\Psi(f_v)}{A_i/4 + 1/L_z},$$
(6.15)

where β depends only on temperature, on the matrix materials, and possibly on the choice of interatomic potential. Note that equilibrium MD simulations with the Green-Kubo theorem could be used to predict phonon dispersion and density of state as well as specific heat and group velocity in silicon nanostructures [189]. However, this falls outside the scope of the present study.

Figure 6.6 plots k_{eff} from the MD simulations as a function of $(1 - 1.5f_v)/(A_i/4 + 1/L_z)$ for all values of porosity, pore diameter, and system length investigated in the present study (Table 6.1). It is remarkable that nearly all data points previously scattered (see Figures 6.3 to 6.4) collapsed onto a single straight line. This indicates that the present model successfully captured the effects of various system morphology simultaneously. Here also, the systems with porosity $f_v = 8\%$ showed relatively large deviations from the other systems. This could be attributed to the fact that the small porosity systems do not satisfy the assumption of the coherent potential model [98], as previously discussed. In addition, Figure 6.6 shows that the effective thermal conductivity k_{eff} for all systems can be linearly related to the present model by using a slope of $\beta = 8.40 \times 10^8 \text{ W/m}^2 \cdot \text{K}$ with a coefficient of determination $R^2 = 0.99$. Note that using the Russell model $\Psi_{Russell}(f_v)$ resulted in $\beta = 7.72 \times 10^8 \text{ W/m}^2 \cdot \text{K}$ with $R^2 = 0.97$.

Figure 6.7 plots the effective bulk thermal conductivity k_{eff} as a function of $(1 - 1.5f_v)/(A_i/4)$ for nanoporous silicon with (a) spherical pores computed in the present study as well as, (b) periodically arranged cylindrical pores [19], and (c) vacancy defects [20] for



Figure 6.6: Effective thermal conductivity k_{eff} as a function of $(1 - 1.5f_v)/(A_i/4 + 1/L_z)$ of all crystalline nanoporous silicon systems simulated at 500 K for porosity f_v ranging between 8% and 38%, pore diameter d_p between 1.74 and 5.86 nm, and system length between 13 and 130 nm. Predictions by Equation (8.1) are also shown with $\beta = 8.40 \times 10^8 \text{ W/m}^2 \cdot \text{K}$.

various values of porosity and pore diameter reported in other MD simulations. Note that the latter used the Tersoff potential instead of the Stillinger-Weber potential. This suggests that the linear relationship between k_{eff} and $(1 - 1.5f_v) / (A_i/4)$ is independent of the choice of potential although the coefficient of proportionality β may not. Also, note that in Lee *et al.*'s study [20], the 0.15% vacancy concentration did not satisfy the ballistic transport assumption and was not included in the plot. Here also, the effective bulk thermal conductivity k_{eff} was inversely proportional to A_i and followed the coherent potential model $(1 - 1.5f_v)$ for the three types of nanostructures considered. The coefficient of proportionality between k_{eff} and $(1 - 1.5f_v)/(A_i/4)$ was found to be $\beta = 5.38 \times 10^8 \text{ W/m}^2 \cdot \text{K}$ and $\beta = 6.26 \times 10^8 \text{ W/m}^2 \cdot \text{K}$



Figure 6.7: Effective bulk thermal conductivity k_{eff} as a function of $(1 - 1.5f_v)/(A_i/4)$ for nanoporous silicon with (a) spherical pores (present study) at 500 K, (b) periodically arranged cylindrical pores at 300 K [19], and (c) vacancy defects [20] for various values of porosity and pore diameter. Predictions by Equation (8.1) are also shown with (a) $\beta = 8.40 \times 10^8$ W/m²·K, (b) $\beta = 5.38 \times 10^8$ W/m²·K, and (c) $\beta = 6.26 \times 10^8$ W/m²·K.

for nanoporous Si with cylindrical pores and vacancy defects, respectively. The difference in the value of β can be attributed to difference in temperature (500 or 300 K), interatomic potential (SW or Tersoff), pore or vacancy shapes, as well as spatial arrangement.

6.4 Conclusions

This study established that the effective thermal conductivity k_{eff} of crystalline nanoporous silicon predicted from non-equilibrium MD simulations was strongly affected by the pore interfacial area concentration A_i , the porosity f_v , and the system's length L_z . In addition, a modified effective medium approximation combining kinetic theory and the coherent potential approximation suggested that k_{eff} was proportional to $(1 - 1.5f_v)$ and inversely proportional to the sum $(A_i/4 + 1/L_z)$. This model agreed with MD simulation predictions for the thermal conductivity of crystalline nanoporous silicon with not only spherical pores (present study) but also with cylindrical pores and vacancy defects, reported in the literature [19, 20]. These results will be useful in designing nanostructured materials with desired thermal conductivity by tuning their morphology for various applications including thermoelectric energy conversion.

Porosity	Pore diameter	Cross-section area	Length	Pore number
%	d_p (mm)	$A_c \; (\mathbf{nm}^2)$	L_z (nm)	Ν
×	1.74	$3.26{ imes}3.26$	13 to 104	4 to 32
×	2.93	$5.43{ imes}5.43$	22 to 109	4 to 20
15	2.17	$3.26{ imes}3.26$	13 to 104	4 to 32
15	2.88	4.34×4.34	17 to 104	4 to 24
27	2.61	3.26 imes 3.26	13 to 104	4 to 32
27	3.48	4.34×4.34	17 to 104	4 to 24
27	4.34	$5.43{ imes}5.43$	22 to 109	4 to 20
27	5.21	$6.52{ imes}6.52$	26 to 130	4 to 20
38	2.93	3.26 imes 3.26	13 to 104	4 to 32
38	3.91	4.34×4.34	17 to 104	4 to 24
38	4.89	$5.43{ imes}5.43$	22 to 130	4 to 24
38	5.86	$6.52{ imes}6.52$	26 to 130	4 to 20

Table 6.1: Summary of simulated crystalline nanoporous silicon systems with various porosity, pore diameter, cross-section area, system length, and pore number.

Nomenclature

a	Lattice constant [m]
A_c	Cross-section area $[m^2]$
A_i	Interfacial area concentration $[m^{-1}]$
C_{v}	Specific heat $[J/kg \cdot K]$
d_p	Pore diameter [m]
f_v	Porosity
G	Shear modulus [GPa]
k	Thermal conductivity $[{\rm W}/{\rm m}{\cdot}{\rm K}]$
K	Bulk modulus [GPa]
l	Dominant phonon mean free path [m]
L_z	System length [m]
m_i	Mass of individual atom i [kg]
n	Number of pores per unit volume $[m^{-3}]$
n_k	Number of atoms in a slice
N	Pore number
q_z''	Heat flux in z-direction $[\mathrm{W}/\mathrm{m}^2]$
R^2	Coefficient of determination
Т	Temperature [K]
v_g	Group velocity [m/s]
v_i	Velocity of individual atom $i~[{\rm m/s}]$

Symbols

α, β, γ	Empirical parameters		
λ	Lamé's elastic constant [GPa]		
ρ	Density $[kg/m^3]$		
τ	Phonon relaxation time [s]		
Ψ	Porosity function		

Subscripts

В	Refers to phonon-boundary scattering
eff	Refers to effective properties
f	Refers to thin film
L	Refers to longitudinal polarization
m	Refers to dense matrix properties
max	Refers to maximum
min	Refers to minimum
MD	Refers to molecular dynamics
Р	Refers to phonon-pore scattering
Т	Refers to transverse polarization
U	Refers to phonon Umklapp scattering
z	Refers to z -direction

CHAPTER 7

Tuning Thermal Conductivity of Nanoporous Si by Surface Passivation

The present chapter explores the use of surface passivation as a way to tune the thermal conductivity of nanoporous crystalline silicon using equilibrium molecular dynamics simulations. The porosity varied from 8% to 38% while the pore diameter ranged from 1.74 to 2.93 nm. Both hydrogen and oxygen passivation were investigated. The vibration spectra of silicon atoms and passivation atoms were discussed to better understand the passivation effect.

7.1 Introduction

In Chapter 6, a scaling law for thermal conductivity of nanoporous crystalline silicon with unpassivated pores was derived by combining kinetic theory and non-equilibrium molecular dynamics (NEMD) simulations [159]. The thermal conductivity k_0 was found to be linearly proportional to $\Psi(f_v)/(A_i/4)$ where f_v is the porosity, $\Psi(f_v) = 1 - 1.5f_v$ corresponds to the coherent potential effective medium approximation [98], and $A_i = 6f_v/d_p$ is the interfacial area concentration for a simple cubic pore arrangement. The pore diameter d_p ranged from 1.74 to 5.86 nm while the porosity f_v varied from 8% to 38%, corresponding to an interfacial area concentration A_i between 0.16×10^9 and 0.78×10^9 m²/m³.

In practice, Si atoms located at the pore surface are chemically passivated. For example, surfaces of porous silicon prepared using electrochemical etching are usually passivated with hydrogen atoms [191]. The hydrogen passivated surfaces, however, are easily oxidized when exposed to atmosphere or moisture, resulting in oxygen passivation. In general, surface passivation in nanostructured materials was found to affect their chemical reactivity [192, 193]. electrical and optical properties [194, 195], as well as their thermal conductivity [83,84, 196]. For example, recent molecular dynamics study showed that hydrogen passivation on the edges of graphene nanoribbons reduced their thermal conductivity by about 40-60% between 100 and 300 K [83,84]. This was attributed to phonon scattering by the hydrogen passivated edges [83,84]. In addition, Lee *et al.* [19] reported the room temperature thermal conductivity of hydrogen passivated nanoporous silicon with cylindrical pores using equilibrium molecular dynamics. The porosity and pore diameter varied from 7% to 38% and from 0.63 to 2.26 nm, respectively. However, the chemical nature of the passivation was not explicitly investigated. Considering the large interfacial area concentration present in nanoporous silicon, the effect of surface passivation may become significant and therefore add another parameter in the quest to tune their thermal conductivity for various applications.

7.2 Analysis

7.2.1 Equilibrium MD simulations

In the present study, the thermal conductivity of both hydrogen and oxygen passivated nanoporous silicon was simulated using equilibrium molecular dynamics (EMD) [16]. Unlike NEMD simulations performed previously [159]. EMD simulations can be used to predict the bulk thermal conductivity directly with a relatively small number of atoms. In addition, dynamic properties such as the phonon density of state can be conveniently calculated [197]. The Tersoff-type potential reported by de Brito Mota *et al.* [198] was used to simulate Si-H and H-H interatomic interactions while another Tersoff-type potential parameterized by Munetoh *et al.* [199] was used for Si-O and O-O interactions. The parameters for Si-Si interactions reported by Tersoff [200] were used for both types of passivated silicon.

7.2.2 Nanoporous Silicon Structures

Figures 7.1(a) and 7.1(b) show the surface bonding structures of hydrogen and oxygen passivation investigated in the present study, respectively. For hydrogen passivation, Si-H bonds were used to terminate the dangling bonds of the Si atoms at the pore surface. For oxygen passivation, Si-O-Si bridge bonds were applied to passivate neighboring surface Si atoms. This passivation method was also used by Lin *et al.* [201] recently to study the band gap of oxygen passivated Si nanonets. As an example, Figure 7.1(c) shows the 3D atomic structure of the simulation domain with 38% porosity. It contained $6 \times 6 \times 6$ unit cells with side length L = 3.258 nm. A spherical pore with diameter d_p was created by removing Si atoms within selected region of the simulation domain. Figure 7.1(d) shows a front view of a thin slice cut through the pore's equator and clearly illustrates surface passivation by hydrogen atoms. Periodic boundary conditions were used in all three directions corresponding to a simple cubic pore arrangement. According to Schelling *et al.* [16] and Lee *et al.* [19], the effect of the simulation domain size was negligible for the systems investigated in the present study. This was also verified by the fact that the simulated thermal conductivity of nanoporous silicon systems at 500 K with one and two pores were identical within the simulation uncertainties. Table 7.1 summarizes the range of porosity f_v , spherical pore diameter d_p , and interfacial area concentration A_i of the different systems investigated.



Figure 7.1: Surface bonding structure for (a) hydrogen passivated and (b) oxygen passivated nanoporous crystalline silicon, along with (c) atomic structure of hydrogen passivated nanoporous silicon with 8% porosity. The green and white spheres correspond to silicon and hydrogen atoms, respectively.

Sample No.	Porosity	Pore diameter	Interfacial area concentration
	f_v (%)	$d_p imes 10^{-9}$ (m)	$A_i imes 10^9 \left({\mathbf{m}}^2 / {\mathbf{m}}^3 ight)$
1	8	1.74	0.28
2	15	2.17	0.42
3	27	2.61	0.62
4	38	2.93	0.78

Table 7.1: Summary of nanoporous silicon systems with spherical pores in simple cubic arrangement for various porosity f_v , pore diameter d_p , and interfacial area concentration A_i .

To account for the surface passivation, hydrogen and oxygen atoms were placed in the vicinity of surface Si atoms at a distance of 1.50 Å and 1.60 Å corresponding to the Si-H and Si-O bond length, respectively [198, 199]. Note that the number of the oxygen atoms was half of that of the hydrogen atoms due to the fact that one oxygen atom was connected to two silicon atoms as shown in Figure 7.1(b). After passivating the pore surface, an energy minimization step was performed to relax the entire structure. Simulations were performed with a time step of 0.05 fs.

7.2.3 Simulation Procedure

Initially, the system was set to equilibrium at a desired temperature by imposing constant number of atoms, volume, and temperature conditions (NVT ensemble) for 1 million time steps. Then, the system was relaxed under constant number of atoms, volume and energy conditions (NVE ensemble) for another 1 million time steps. Finally, the thermal conductivity was estimated based on the Green-Kubo relation expressed as [16],

$$k = \frac{1}{3Vk_BT} \int_0^{\tau_M} \langle J(0)J(t)\rangle dt, \qquad (7.1)$$

where V is the volume of the system, $k_B = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant, T is the temperature, $\langle J(0)J(t)\rangle$ is the time-averaged heat current autocorrelation function (HCACF), and τ_M is the maximum length of correlation time window. The details of the Green-Kubo methodology can be found in Ref. [16] In the present study, the HCACF decayed with time and oscillated around zero when t > 30 ps for nanoporous crystalline silicon. Therefore, the integral in Equation (7.1) converged for $\tau_M > 30$ ps. The integral was averaged over numerous time windows with τ_M ranging between 30 ps and 80 ps. Then, it was used to determine the thermal conductivity from Equation (7.1). In addition, the total simulation time should be considerably larger than τ_M in order to achieve good statistical averaging of the HCACF and accurate thermal conductivity predictions [16]. We found that the thermal conductivity reached a plateau when the total simulation time was 2 ns or larger. Therefore, a total simulation time of 2 ns, corresponding to 40 million time steps, was adopted for all simulations. Finally, for each system and temperature, the average thermal conductivity and the associated uncertainty corresponding to 95% confidence intervals were estimated from 6 independent simulations.

7.3 Results and Discussion

7.3.1 Dense Crystalline Silicon

For validation purposes, the thermal conductivity of dense (nonporous) crystalline silicon denoted by k_b was simulated and found to be 120 ± 13 , 79 ± 9 , and 57 ± 6 W/m·K at 500, 750, and 1000 K, respectively. These values were in good agreement with NEMD results recently reported by Abs da Cruz *et al.* [202] Note that, according to Volz and Chen [174], quantum corrections are negligible for crystalline silicon systems beyond 500 K. Note that for dense silicon, the time step was 0.55 fs and the total simulation period was 6.6 ns, as suggested by Schelling *et al.* [16]

7.3.2 Passivated Nanoporous Crystalline Silicon

Figures 7.2(a) and 7.2(b) show the thermal conductivity of hydrogen and oxygen passivated nanoporous crystalline silicon, denoted as $k_{HP}(T)$ and $k_{OP}(T)$, as a function of temperature from 500 to 1000 K, respectively. The thermal conductivity of unpassivated nanoporous silicon $k_0(T)$ was also plotted for comparison purposes. It is evident that thermal conductivity of all nanoporous silicon systems decreased with increasing porosity. For example, thermal conductivity of unpassivated nanoporous silicon at 500 K decreased from 9.11 ± 1.32 to 1.51 ± 0.36 W/m·K when porosity increased from 8% to 38% at 500 K. Overall, the presence of nanopores reduced thermal conductivity of dense crystalline silicon by about one order of magnitude at all temperatures. The thermal conductivity of nanoporous crystalline silicon has been shown to decrease not only due to the loss of material, taken into account by effective medium approximation, but also by strong phonon scattering at pore surface [19, 159, 167]. In fact, we verified that the scaling law $k \propto (1 - 1.5 f_v)/(A_i/4)$ previously reported [159] was also applicable to the passivated nanoporous crystalline silicon.



Figure 7.2: Thermal conductivity of (a) hydrogen passivated and (b) oxygen passivated nanoporous crystalline silicon, denoted by $k_{HP}(T)$ and $k_{OP}(T)$, as a function of temperature from 500 to 1000 K, respectively. Thermal conductivity of unpassivated nanoporous silicon $k_0(T)$ was also shown for comparison.

In addition, Figures 7.2(a) and 7.2(b) show that the simulated thermal conductivity for passivated and unpassivated systems decreased monotonically with increasing temperature from 500 to 1000 K for porosity of 8% and 15%. This can be attributed to the fact that phonon Umklapp scattering, caused by anharmonic interactions, increased with increasing temperature. However, the thermal conductivity of systems with porosity of 27% and 38% did not show strong temperature dependence. This can be attributed to the fact that

strong phonon scattering by pores boundaries and passivation layers dominated over Umklapp scattering. Finally, it is evident that oxygen passivation reduced thermal conductivity of nanoporous crystalline silicon while hydrogen passivation had a lesser effect.

Figures 7.3(a) and 7.3(b) plot the ratios $k_{HP}(T)/k_0(T)$ and $k_{OP}(T)/k_0(T)$ as a function of porosity at 500, 750 and 1000 K, respectively. Note that the increasing error bars with porosity was caused by the small value of $k_0(T)$ for systems with large porosity, according to standard error propagation analysis. Increasing the number of runs from 6 to 10 or 15 reduced the error bars only slightly while the average thermal conductivity remained nearly the same. It is evident that the presence of hydrogen passivation reduced the thermal conductivity at 500 K by 14% to 24% depending on the porosity. Similarly, oxygen passivation reduced the thermal conductivity at 500 K by 34% to 52%. The reduction was attributed to phonon scattering by the passivated surfaces, including the Si atoms at the pore surface and passivation atoms. In addition, hydrogen passivation did not have a statistically significant effect on the thermal conductivity at 750 K and 1000 K as shown in Figure 7.3(a). In fact, hydrogen passivation effect was masked by strong phonon Umklapp scattering at high temperatures. However, reduction in thermal conductivity was observed at all temperatures for oxygen passivated nanoporous silicon, except for films with porosity of 38% at 1000 K. Finally, note that phonon leakage, such as that observed in Si supported graphene sheets and resulting in low thermal conductivity [80–82], was not expected in the present nanoporous crystalline silicon since the pores were empty.

7.3.3 Vibrational Spectra

To further understand the origin of thermal conductivity reduction in passivated nanoporous silicon, we considered the vibrational spectra obtained by Fourier transform of the velocity autocorrelation function [197]. Figure 7.4(a) shows the vibrational spectra of the hydrogen passivated, oxygen passivated, and unpassivated Si atoms located at the pore surface in the nanoporous system with 8% porosity at 500 K. The vibrational spectrum or the phonon density of states of bulk silicon is also shown as a reference. The peaks present at frequencies



Figure 7.3: Ratios $k_{HP}(T)/k_0(T)$ and $k_{OP}(T)/k_0(T)$ as a function of porosity at 500, 750 and 1000 K, respectively. Here, $k_{HP}(T)$, $k_{OP}(T)$, and $k_0(T)$ denote the thermal conductivity of hydrogen passivated, oxygen passivated, and unpassivated nanoporous silicon, respectively.

less than 12 THz and around 13-18 THz for all spectra correspond to acoustic and optical modes, respectively [203,204]. Note that acoustic phonons contribute to heat transport unlike optical phonons which mainly affect optical properties [4]. It is evident that the acoustic modes of both passivated and unpassivated surface Si atoms shifted to lower frequency compared with that of the bulk Si atoms. This can be attributed to the fact that the surface Si atoms have fewer Si-Si bonds than the bulk Si atoms and therefore have less stiff bonds, resulting in the softening of the phonon frequency [203, 204]. In addition, the amplitude of the vibrational spectra in the acoustic branch of the hydrogen and oxygen passivated Si atoms were smaller than those of the unpassivated Si atoms but still larger than those of the bulk Si atoms at the pore surfaces [203, 205] and (ii) the surface Si-O and Si-H bonds were different from the Si-Si bonds in bulk crystalline matrix. For example, the average lengths of Si-O and Si-H bonds at the pore surface were 1.6 μ m and 1.4 μ m while it was 2.3 μ m for Si-Si bonds in the matrix. Finally, the difference in vibrational spectra between bulk and passivated surface Si atoms also suggested that

they had different lattice structures and therefore a lattice mismatch near the pore surface, resulting in additional phonon scattering.



Figure 7.4: (a) Vibrational spectra of hydrogen passivated, oxygen passivated, and unpassivated surface Si atoms in nanoporous silicon at 500 K with 8% porosity. The phonon density of states of bulk crystalline silicon is also shown as a reference. (b) Vibrational spectra of surface hydrogen and oxygen atoms in nanoporous silicon at 500 K with 8% porosity.
Moreover, Figure 7.4(b) shows the vibrational spectra of hydrogen and oxygen atoms in the same nanoporous system with 8% porosity at 500 K. On the one hand, the oxygen atoms vibrated primarily at frequencies less than 15 THz and the amplitudes peaked around 4 and 8 THz. It is evident that the vibrational spectrum of the oxygen atoms overlapped with those of the Si atoms at low frequencies populated by acoustic phonons. This suggested that the oxygen atoms interacted and exchanged energy primarily with silicon acoustic phonons through stretching-like vibrations of Si-O bonds [206]. The same mechanism was also found responsible for the thermal conductivity reduction in water-filled carbon nanotubes [207,208] as well as in hydrogen functionalized graphene sheets [196]. On the other hand, Figure 7.4(b) shows that the hydrogen atoms vibrated primarily at frequencies larger than 15 THz and had peak amplitudes around 20 THz. Therefore, interaction and energy transfer between silicon and hydrogen atoms were reduced compared with oxygen passivation. Thus, the thermal conductivity of nanoporous Si was less affected by hydrogen passivation. Note that these results and discussion also applied to other systems and temperatures investigated.

Moreover, the vibrations of the passivation atoms at high frequencies also affected the optical modes of surface Si atoms. For example, the peaks around 15, 19, and 23 THz in the vibrational spectra of passivated surface silicon atoms [Figure 7.4(a)] were caused by energy transfer of the vibrational modes of the oxygen and hydrogen passivation atoms through Si-H and Si-O bonds as observed in Figure 7.4(b) for the same frequencies.

7.3.4 Validation of the Scaling Law

Figures 7.5(a) and 7.5(b) plot the thermal conductivity of hydrogen and oxygen passivated nanoporous silicon k_{HP} and k_{OP} as a function of $(1 - 1.5f_v)/(A_i/4)$ at 500, 750, and 1000 K, respectively. They both show that the data points aligned onto a straight line for each temperature.



Figure 7.5: Simulated thermal conductivity of hydrogen and oxygen passivated nanoporous silicon k_{HP} and k_{OP} as a function of $(1-1.5f_v)/(A_i/4)$ at 500, 750, and 1000 K, respectively. The lines are linear fittings to the data.

7.4 Conclusions

To conclude, the present study shows that oxygen passivation reduced the thermal conductivity of nanoporous crystalline silicon by 34% to 52% while hydrogen passivation resulted in a 14% to 24% reduction at 500 K. The hydrogen passivation effect diminished with increasing temperature. Physical mechanism responsible for the thermal conductivity reduction was investigated using the vibrational spectra of the passivation atoms and silicon atoms. Unlike for hydrogen passivation, the vibrational spectrum of oxygen atoms overlapped with those of silicon atoms at low frequencies, indicating strong interactions and energy exchange between silicon and oxygen atoms. These results can be used in designing nanostructured silicon with desired thermal conductivity by tuning not only their morphology but also their surface passivation.

Nomenclature

A_i	Interfacial area concentration $[m^{-1}]$
d_p	Pore diameter [m]
f_v	Porosity
$\langle J(0)J(t)\rangle$	Heat current autocorrelation function
k	Thermal conductivity $[{\rm W}/{\rm m}{\cdot}{\rm K}]$
k_B	Boltzmann constant [J/s]
L	Simulation domain side length [m]
Т	Temperature [K]
V	Simulation domain volume $[m^3]$

Symbols

$ au_M$	Maximum length of correlation time window [s]
Ψ	Porosity function

Subscripts

b	Refers to bulk dense crystalline silicon
HP	Refers to hydrogen passivated nanoporous silicon
OP	Refers to oxygen passivated nanoporous silicon
0	Refers to unpassivated nanoporous silicon

CHAPTER 8

Conclusions and Future Work

This chapter summarizes the main contributions of the present study and makes recommendations for future work expanding on results reported in this thesis.

8.1 Main Contributions

The present study not only reported thermal conductivity of nanoporous thin films with tunable structures but also shed light on the complex relationship between nanostructures and their thermal transport properties. Specifically, the major contributions of this thesis can be summarized as follows:

For the first time, accurate cross-plane thermal conductivity of ordered mesoporous titania and silicon thin films as well as pure silica MFI and MEL zeolite thin films with various structures was reported between 25 and 315 K. Detailed characterization of all synthesized films was systematically performed. The evaporation-induced self-assembly synthesis methods enable one to finely control the structure of the mesoporous thin films, such as porosity, pore size, pore arrangement, wall thickness, and crystallinity, by using different polymer templates, concentrations, and process temperatures. This was illustrated with mesoporous titania and silicon. Pure silica zeolite thin films were also produced by either *in-situ* growth or by spin coating a zeolite nanoparticle suspension onto substrates followed by crystal growth upon heating. Their crystallinity and porosity can also be tuned by using different crystal growth time. The experimental data are valuable for theoretical and numerical model validation as well as for thermal engineering design of energy systems and MEMS devices.

Physics-based models combining phonon transport theory and effective medium approximations were developed to interpret the measured data. The models were able to account for the film porosity and phonon scattering by defects, pores, nanocrystal grain boundaries, and Umklapp scattering. These models successfully captured the measured data and they can be easily modified to predict thermal conductivity of other nanostructured dielectric or semiconductor materials. The thermal conductivity of all synthesized films increased monotonically with temperature between 25 and 315 K. At low temperatures, the nanoporous films behaved like amorphous or strongly disordered materials and their thermal conductivity was proportional to T^n with n varied between 1 and 2.3. At high temperatures, the thermal conductivity increased slowly with temperature or reached a plateau due to strong phonon Umklapp scattering and the saturation of phonon modes.

The presence of pores in *amorphous* mesoporous thin films had a purely geometrical effect and reduced the thermal conductivity by reducing the cross-sectional area through which heat can diffuse. By contrast, in *crystalline* mesoporous thin films the presence of pores and of nanocrystals increased phonon scattering and therefore reduced thermal conductivity. In addition, the film thickness generally did not affect the measured thermal conductivity. Indeed, phonon scattering by pores and by nanocrystal grain boundary dominated over boundary scattering and were identified as the dominant scattering mechanisms for nanoscale energy transport in the synthesized nanoporous films. For example, the thermal conductivity of nanocrystal-based mesoporous titania film was about 40% less than that of the polycrystalline mesoporous films. It was attributed to the fact that smaller crystal size and poorly interconnected nanocrystal boundaries caused stronger phonon scattering. In addition, the zeolite films were found to have thermal conductivity smaller than that of amorphous silica due to strong phonon scattering by micropores. Finally, the ordered meosporous nanocrystalline silicon thin films had thermal conductivity 2-3 orders of magnitude smaller than single crystal silicon mainly due to strong phonon scattering by pores and by nanocrystal grain boundary in the dense matrix.

In addition, this study established that the effective thermal conductivity k_{eff} of crystalline nanoporous silicon was not only a function of porosity f_v expressed by an effective medium approximation but also strongly affected by the interfacial area concentration A_i and the system's length L_z . Indeed, a modified effective medium model combining kinetic theory and the coherent potential approximation suggested a scaling law expressed as,

$$k_{eff} \propto \frac{\Psi(f_v)}{A_i/4 + 1/L_z}.$$
(8.1)

This scaling law was obtained using MD simulations for the thermal conductivity of crystalline nanoporous silicon with not only spherical pores (present study) but also with cylindrical pores and vacancy defects as reported in the literature [19,20]. It is of particular interest for tuning thermal conductivity since it quantifies the complex nanostructure-properties relationship.

Finally, while tuning the various morphological parameters was shown to be effective in controlling thermal conductivity, it may cause unwanted changes to other properties. For example, by increasing porosity and/or making the dense matrix nanocrystalline, both thermal and electrical conductivity may be reduced as well as mechanical strength. The present study demonstrated that surface passivation can add another parameter to reduce thermal conductivity. To do so, there should be strong acoustic vibrational modes coupling between surface atoms and passivation atoms or molecules. For example, oxygen passivation was shown to reduce the thermal conductivity of nanoporous crystalline silicon. In addition, the effect of passivation reduced with temperature because of increasing contribution of Umklapp scattering.

These results are useful to design novel nanostructured materials with desired thermal conductivity for various applications. For example, in order to reduce thermal conductivity of a nanostructured material, one can (i) make the matrix either amorphous or nanocrystalbased, (ii) use smaller nanocrystal grain size, (iii) increase porosity, (iv) increase interfacial surface area concentration, and/or (v) passivate the nanostructure.

8.2 Future Work

This section presents several recommendations and suggestions for future work.

New Knowledge

- The copolymer templated ordered mesoporous thin films made of transition metal oxide (e.g., RuO₂, TiO₂, MnO₂, V₂O₅, and Nb₂O₅) have been proposed as electrodes for supercapacitors thanks to their large surface area per unit volume as well as to surface redox reactions with lithium ions (Li⁺) in an organic electrolyte [22,23]. Under operating conditions, the mesoporous electrodes are impregnated with electrolytes [23]. Knowing the thermal properties of electrolyte filled mesoporous thin films is of particular interest for the thermal management of such supercapacitors. To do so, experimental measurements of the thermal conductivity of mesoporous thin films filled with various electrolytes could be performed. Physical modeling and numerical simulations should also be performed, in conjunction with experimental study, to better understand how (i) the presence of liquid electrolyte, (ii) the formation of the electrical double layer and (iii) the redox reactions affect thermal transport in the nanostructured electrodes.
- The present study investigated the effect of surface passivation on the thermal conductivity of nanoporous silicon. Hydrogen and oxygen passivation were simulated but there exists many other types of surface passivation and their effects on thermal transport properties have yet to be explored. For example, organic monolayer of alkyl (Si-C-C), alkenyl (Si-C=C), and alkoxyl (Si-O-C) were used to passivate oxygen free nanostructured silicon [209]. Unlike hydrogen passivation, they are both thermally and chemically robust [210]. On absence of intervening SiO₂ layer, these monolayers have direct coupling between any organic functionality and the silicon substrate [209, 211, 212]. Knowledge of the effect of these organic monolayer passivation on thermal properties would be useful for device design and their thermal management.

New Experimental Data

• As discussed, porous silicon is a promising high temperature thermoelectric material. Its operating temperature typical ranges from 573 to 1273 K [67]. In Chapter 5, thermal conductivity of ordered mesoporous silicon thin films was reported between 25 and 315 K. Therefore, high temperature thermal conductivity measurements combined with electrical conductivity and Seebeck coefficient measurements are still necessary to evaluate their thermoelectric performance. Validity of the physics-based model developed in Chapter 5 should also be examined for high temperatures.

• The scaling law derived from MD simulations, relating thermal conductivity of nanoporous crystalline silicon to its porosity and pore interfacial area concentration, needs to be experimentally validated. Experimental measurements can be performed using a special type of nanostructures called phononic crystals. Just as photonic crystals can be used to manipulate electromagnetic waves (light), phononic crystals with nano-size inclusions or pores in a lattice with single, double, or triple periodicity can be used to manipulate acoustic waves, which carry heat [153,213]. Their applications include filters, vibration/sound insulations, and waveguides. Such materials have a structure similar to those in our MD simulations. The challenge may lie in the fabrication techniques of phononic crystals and experimental techniques to precisely determine their thermal conductivity.

Modeling Tools

- In Chapter 4, the temperature evolution of the thermal conductivity of MFI zeolite was captured by the Callaway model. The present level of modeling was sufficient to interpret the experimental data and identify the key structural parameters that control heat transfer. However, more detailed modeling should be performed by considering the detailed dispersion relation in MFI zeolite and by accounting for phonon polarization. The complete phonon dispersion relation can be calculated based on lattice dynamics, as reported by Greenstein *et al.* [13] and Hudiono *et al.* [132]. Such model can offer more insight into the thermal transport in zeolite. For example, the thermal conductivity spectrum can be derived to illustrate the contribution of phonons with different frequency to the energy transport.
- The dense matrix of nanoporous silicon simulated in MD simulations were monocrys-

talline. Experimentally, the matrix of highly-ordered mesoporous silicon thin films were nanocrystalline. Thus, experimental data for thermal conductivity could not be directly compared with MD simulation results. Future study should therefore consist of developing new MD simulation tools to create and account for the nanocrystals in the dense matrix in addition to the presence of the pores. Phillpot *et al.* [214, 215] developed a method to prepare nanocrystalline structures in MD simulations. First, small pre-oriented single-crystal seeds were embedded into a melted system of the same material. The system was subsequently cooled below the melting point to enable crystal growth under an applied external pressure. The resulting nanocrystalline material was composed of large perfect-crystal regions separated by well-defined grain boundaries [214, 215]. Similar approach could be used for preparing mesoporous nanocrystalline structure but with an additional step to create pores. The challenge may lie in the realistic modeling of the randomly oriented nanocrystals surrounding the nanopores which are connected through sub-nanometer necks.

Nomenclature

A_i	Interfacial area concentration $[m^{-1}]$
d_p	Pore diameter [m]
f_v	Porosity
k	Thermal conductivity $[\mathrm{W}/\mathrm{m}{\cdot}\mathrm{K}]$
L_z	System length [m]
Т	Temperature [K]

Symbols

Subscripts

eff	Refers	to	effective	properties
$\bigcirc j j$	1001010	00	011000110	properties

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