Size Effects on Thermal Transport in Materials and Interfaces

A Dissertation in

Mechanical Engineering

by

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ABSTRACT

With the ever-continuing miniaturization of electronics and micro/nano electromechanical systems, materials length-scale is reduced to a level where they exhibit physical properties significantly different from the bulk values. Emergence of novel materials with variation in parameters like thickness, composition, density, porosity etc., has made it possible to witness exceptional physical properties. Significant research efforts have been directed towards the size dependency of materials’ ability to carry current, heat or mechanical load. This dissertation focuses on thermal properties since very large scale integration of electronics or sensors implies a rapid increase in the heat dissipation density and temperature. Accurate thermal characterization of the materials and their interfaces is essential for a reliable design. It is also essential to design efficient heat removal channels for thermal management of electronics. In this dissertation, we argue that if size effect can breakdown physical laws in individual domains, it can also couple the various domains. Such length-scale induced multi-domain coupling can open novel transduction schemes. For example, thermal properties of materials can be tuned by application of mechanical strain. This dissertation is aimed at studying the size effect on thermal transport phenomenon in materials and the coupling with other physical domains. The objective of this research is to experimentally study the influence of these parameters on thermal properties of solids and to explore the size-induced coupling between physical domains such that these materials can be actively tuned to obtain the desired properties.

Our experimental framework is based on an Infrared microscopy based technique that maps the temperature field in microfabricated specimens and then perform energy balance to determine its thermal conductivity. This technique was applied to materials with low dielectric constant (low-
that are used as inter-layer dielectrics to enable faster communication in electronics by reducing the delay time. Typically, lower dielectric constant is achieved by making the material porous, which also lowers the thermal conductivity. The low thermal conductivity measurement is particularly challenging because only high resolution temperature mapping can quantify the thermal gradient. We conducted a systematic study on thermal conductivity of these materials using simple fabrication process. It was found that the thermal conductivity decreases with porosity and increases with density and the values obtained are consistent with the empirical models in the literature.

Interfaces between dissimilar materials are ubiquitous in electronic devices. From a thermal transport standpoint, the interface is as important as the constituent material. Interfacial Thermal Resistance (ITR) is the property that determines the quality of an interface. ITR is one of the most challenging measurands in experimental heat transfer, particularly for micro and nanoscale thin films. It is also the dominating quantity in thermal management of microelectronic and energy conversion devices. We developed a novel technique that exploits the size dependence of thermal resistance in thin films to magnify the temperature drop at the interface, which is then measured with infrared thermometry. We show that orders of magnitude amplification in interfacial temperature drop is possible by making the specimen freestanding, which facilitates the measurement. We present experimental results on metal–dielectric interfaces involving aluminum, copper, silicon di-oxide and hafnium oxide for validation of the technique. This technique is further extended to measure the ITR of interface between silicon and carbon doped oxide (CDO) which is a low dielectric constant (low-k) and highly porous material albeit using a different fabrication process.
In this dissertation, we also present experimental evidence that thermal conductivity is coupled with mechanical strain in thin metal films. This is contrary to the classical understanding that electrons are not scattered appreciably by defects or deformation. Or in other words, metals are not expected to show strain dependent thermal transport. We hypothesize that for grain sizes below the electron mean free path, mechanical deformation mechanism and volume fraction of grain boundaries are drastically different from the bulk. Unlike dislocations (bulk scale deformation mechanism), grain boundaries strongly scatter electrons. Therefore, the very large volume fraction of grain boundaries in nanocrystalline metals lead to thermal scattering reducing the thermal conductivity. To investigate this hypothesis of grain size-induced thermo-mechanical coupling, the thermal conductivity of 100-nm-thick freestanding nanocrystalline zirconium (Zr) films was measured as a function of externally applied mechanical strain. Experimental results show strong mechanical strain–thermal conductivity coupling, thermal conductivity of Zr film dropped from 20 to 13 W/m-K with an increasing strain from 0 to 1.24 %. Thermal conductivity of Zr film is also measured as a function of average grain size ranging from as-deposited 10 nm to as grown 250 nm. The results show that for grain sizes above 10 nm, mechanical strain has no influence over thermal conductivity, which supports the proposed hypothesis.

Another key contribution of this dissertation is to exploit the length-scale effects of thermal transport to advance the performance of real-life applications. This is demonstrated with a thin film based Thermoelectric Energy Conversion (TEC) design with a transformative shift from the current state of art commercially available TEC devices. This design applies in-plane thermoelectric elements compared to the universal practice of cross-plane ones. The size dependent thermal resistance and heat transfer coefficient results in very high temperature differential across a thermoelectric element. It also obviates the requirement of forced cooling
(which itself demands energy expenditure) to maintain the cold end temperature. Preliminary results show that the device operates at ~ 10% Carnot efficiency at 100 °C hot surface temperature.

We conclude the dissertation by demonstrating some experimental evidence on heat super conduction at room temperature in a bulk material viz., Lithium Niobate (LiNbO₃). Ballistic mode of heat transport happens when the phonon scattering is very less or almost absent in the material. The heat carriers are propagated from hot end to the cold end without any gradient in the material. Unfortunately, this kind of heat transport is only seen at ultra-low temperatures (around 4K) or in nanoscale structures at room temperature. Numerous thermal engineering applications including heating, cooling, energy conversion etc. would be very efficient if the heat transfer were ballistic. We present a series of experiments based on Infrared thermography to support this phenomenon in Lithium Niobate at room temperature.

To summarize, this dissertation introduces a new experimental technique for thermal characterization of materials and interfaces at small length scales. It also probes the length scale induced coupling between multiple physical domains. Though the majority of it is fundamental in nature, a segment of this dissertation deals with developing a novel thermoelectric generator that has a direct application. The other results obtained in this dissertation will enhance the understanding of thermal properties of materials and act as groundwork for future endeavors in this field.
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DEDICATION

I dedicate this dissertation to my family and country
1. Introduction

Nanotechnology involves materials and interfaces with size on the order of nanoscale displaying size dependent physical properties. It was heralded by modern microelectronics which witnessed transistors [1] replacing vacuum tubes and their number in integrated circuits has doubled every two years as predicted by Moore [2]. Microelectromechanical system (MEMS) technology was inspired by the microelectronic revolution and to an extent, by the awareness provided by Feynman [3] in his pioneering talk. Miniaturization of systems has continued since then driven by advances in science, engineering and need for faster and smaller devices. This has resulted in discovery of novel materials with excellent electrical and mechanical properties like carbon nanotubes (CNTs) [4], nanowires and a new class of two-dimensional materials such as graphene [5], monolayer molybdenum disulphide with very high potential applications having a direct impact on the science & technology of materials. Investigation of these phenomena and comprehending the new physics emerging at these length scales has been the focus of state of the art interdisciplinary research in materials and device engineering.

1.1. Length scale effect

Physical properties of materials at micro/nano scale differ significantly from their bulk scale behavior which is commonly known as ‘size effect’ in the scientific community. The variation of mechanical [6-16], thermal [13, 14, 17-27], electrical [28-30] and optical [28] properties of materials with size points out the contrast with bulk scale phenomenon. Size dependent aspects like deformation mechanism, energy distribution in the surface shell, high surface area to volume ratio are some of the underlying physics that explain the unusual behavior. Trends observed with
size are not universal and depend highly on the material, geometry and boundary conditions. For example, it is dominantly observed that the Young’s modulus increases with decrease in size [6, 15, 16], yet a decrease is also observed in some cases [31, 32] which is mainly attributed to particular surface effects.

Electrical properties of thin films and materials at small scale are observed to deviate from the bulk value, albeit at a different scaling of length. With the number of transistors increasing almost every day, theirs as well as the interconnect size is approaching the mean free path of electrons. Scattering at grain boundary and surface are known to increase the electrical resistivity, which requires extrapolation of the classical models (such as Mayadas and Shatzkes [33]) to the extremely small scales. As one approaches smaller wire dimensions, the mean grain size reduces increasing the number of grain boundaries eventually resulting in higher electrical resistivity.

Similarly, thermal properties of materials at small scales differ from their bulk values. Figure 1.1 shows the trend of thermal conductivity of silicon with temperature in silicon thin films [18] and nanowires [23]. It is evident from the figure that the thermal conductivity is much lesser than the bulk value and this is attributed to enhanced phonon scattering at grain boundaries and imperfections.

1.2. Thermal transport in nanoscale materials

While electrical or electronic properties of thin films and one-dimensional nanostructures are studied very extensively, size dependence of thermal transport is less understood, primarily because of the challenges associated with thermal measurements at the smaller length scales.
Phonons are the main heat carriers in semiconductor and dielectric materials while electrons carry the larger fraction of heat in metals. A phonon is a quasi-particle representing the quantum of lattice vibrations in an elastic solid just like a photon is for electromagnetic energy. When solids shrink to nanometer range, the thermal transport phenomenon by phonons is altered due to effects like boundary scattering, modifications in the phonon dispersion relation and quantization of phonons. Thermal conductivity at small size scales is mostly observed to be lesser in value than the bulk crystalline solids due to enhanced boundary scattering of phonons.

Figure 1.1 Variation of thermal conductivity of silicon with temperature in (a) thin films [18] and (b) nanowires [23]

Different possible scattering mechanisms in doped silicon, that become more prominent in other nanoscale materials too, are discussed by Asheghi et al [34] and shown in Figure 1.2. Phonons interact with other phonons, lattice defects, crystal boundaries, dopant atoms and these events are typically referred as scattering processes. These scattering processes are classified as N-(normal) process (phonon momentum is conserved) and Umklapp process (phonon momentum is not
conserved). The average distance they travel between each scattering event is called the mean free path. The phonon mean free path varies in each solid and with its temperature.

![Phonon scattering mechanisms in doped Silicon](image)

Figure 1.2 Phonon scattering mechanisms in doped Silicon [34]

Phonon transport in these solids has three possible mechanisms: a) ballistic transport i.e. the phonons travel through the solid without any interaction, b) second sound where the energy transport is a wave like phenomenon; this happens when the phonon momentum is conserved during most of the scattering process and c) diffusion which is observed in almost all the bulk materials. The ballistic transport and second sound are observed at very low temperatures and in materials of ultra-high purity. When the characteristic size of the solid is much larger than the mean free path of the phonon, which is generally the case in most of the heat conductors, there is massive scattering and the heat flow is diffusive. In nano-systems, mean free path of phonons is comparable to the geometric (thickness, diameter) or microstructural (grain size) size of the materials, heat conduction contains a major ballistic part [35-37]. Phonon propagation in solids can be viewed similar to gas molecules in a space. Hence, kinetic theory is applicable for the phonon gas and it relates thermal conductivity of the material, $\kappa$, to its other properties as
\[ \kappa = \frac{1}{3} C v \lambda \]  

(1.1)

C is the specific heat per unit volume of the material, \( v \) is the speed of sound in the material and \( \lambda \) is the phonon mean free path. In classical physics, Fourier’s law of heat conduction governs the heat transport by assuming local thermal equilibrium and reckons the heat flow to be diffusive in nature. It defines that the heat flux vector \( \mathbf{q} \) is proportional to the temperature gradient \( \nabla T \) in the material and is given by Equation 1.2.

\[ \mathbf{q} = -\kappa \nabla T \]  

(1.2)

Computational studies based on Boltzmann transport equation (BTE) and Molecular Dynamics (MD) simulation [38, 39] are also used extensively to predict the thermal transport behavior in nanoscale materials. BTE is a generic transport equation, and is not just restricted to phonons, which is given by

\[ \frac{\partial f}{\partial t} = \mathbf{v}_g \cdot \nabla f + \frac{\partial \mathbf{k}}{\partial t} \cdot \nabla_k f = \left| \frac{\partial f}{\partial t} \right|_{\text{collision}} \]  

(1.3)

\( f \) is the phonon distribution function dependent on position vector \( \mathbf{r} \), time \( t \), wave vector \( \mathbf{k} \) of the phonons. \( \mathbf{v}_g \) is the group velocity vector of phonons which is defined as

\[ \mathbf{v}_g = \frac{\partial \omega}{\partial \mathbf{k}} \]  

(1.4)

\( \omega \) is the phonon frequency. The right hand side (RHS) of Equation 1.3 denotes the change in the phonon distribution due to the collisions. MD simulation is another approach to understand thermal transport at micro/ nano scale and gives insight into the underlying physics. It involves solving the Newtonian equation to obtain the position field of each atom in the solid. Figure 1.3
shows the effect of film thickness and grain size on thermal conductivity in nanocrystalline Argon ad yttria-stabilized zirconia.

Figure 1.3 (a) Thermal conductivity of Argon nanofilms with their thickness [39] and (b) Thermal conductivity versus grain size at 25K and 480K in nanocrystalline yttria-stabilized zirconia [40] (Reprinted from [40] with permission from Elsevier)

Phonon scattering at the grain boundaries is found to be the most dominating factor that reduces the thermal conductivity in a nanocrystalline material that leads us to the term ‘Kapitza resistance’ which is basically the thermal resistance at the boundary either between two grains or the interface between two materials. The relation between effective thermal conductivity of nanocrystalline material, $\kappa_{\text{eff}}$, and grain boundary thermal (or Kapitza) resistance $R_k$ is suggested as [40]

$$\kappa_{\text{eff}} = \frac{\kappa_o}{1 + \kappa_o R_k d^{-1}}$$  \hspace{1cm} (1.5)
where \( \kappa_0 \) is the bulk thermal conductivity and \( d \) is the characteristic grain size. The inverse of Kapitza resistance is called as the Kapitza conductance. The Kapitza resistance is observed to vary with the grain size and is smaller in value for smaller grains in nanocrystalline Argon [38].

The total thermal resistance \( (R_{pol}) \) in nanocrystalline solids constitutes of two parts: intragranular resistance \( (R_{intra}) \) and intergranular resistances \( (R_{K/d}) \) and their dependence on grain size for nanocrystalline diamond is studied by Dong et al [41] and the trend is shown in Figure 1.4

![Figure 1.4 Grain-size dependence of thermal resistance in nanocrystalline diamond [41] (Reprinted from [41])](image)

Besides the grain boundaries, interfaces between dissimilar materials offer an impedance to thermal transport across them. Even with a perfect contact between the materials, factors like acoustic impedance mismatch, crystal orientation mismatch give rise to a probability that the phonon either gets reflected back or transmitted across the interface. The first measured
interfacial resistance was reported by Kapitza [42] while working with liquid Helium. It is essentially a proportionality constant that relates the differences in the densities and phonon propagation speeds in the two materials to measurable terms such as heat flux, \( q \), across an interface and the temperature drop \( T_{\text{drop}} \) associated with that interfacial region as follows,

\[
R_k = \frac{T_{\text{drop}}}{q}
\]  

(1.6)

1.3. Measurement of thermal properties at nanoscale

Accurate characterization of thermal properties at the nanoscale is very challenging but is essential and forms keystone to the design of heat dissipating devices. Controlled thermal excitation in a material, heat loss to the surrounding boundary conditions and probing the response to a thermal excitation are the main challenges encountered in experimental techniques for thermal characterization of nanoscale materials. The biggest source of error is the heat lost to the surrounding, which can be the ambient medium or a solid substrate. The heat loss mechanism from nanoscale solid structures to the surrounding air is very different from the classical notion of advection dominated heat transfer. Buoyancy forces at the smaller scales are too small to overcome the forces of viscous drag which oppose the convective motion. When a heated microstructure is suspended in air, the dominant mode is conduction through the air molecules [43]. When the material thickness shrinks down to extremely small dimensions, the penetration of thermal excitation often goes beyond the material into the substrate. Such cases present additional complexities of accounting for the heat losses into the substrate into the modeling or the need for testing equipment with high range of operating parameters that can be expensive or infeasible. Significant amount of research in the last couple of decades made it possible to develop several technologies for measuring the thermal properties of thin films.
The $3\omega$ is a transient technique initially developed for measuring the thermal conductivity of amorphous solids [44]. In this technique, a metal line pattern with four pads is deposited on the sample material. The metal line acts as both the heater and temperature sensor. A current of frequency $\omega$ induces a temperature wave with fluctuations at $2\omega$ to diffuse into the substrate. Measuring the electrical resistance of the metal line extracts its temperature amplitude owing to its temperature dependence. $3\omega$ or the third harmonic of the output voltage along the metal line gives knowledge about the thermal properties of the sample material. This technique has been extended to measure in-plane thermal conductivity and interfacial thermal resistance of freestanding thin films [45, 46]. For thin films on a substrate, it is essential that the penetration depth should be lesser than the film thickness for the heat wave to be confined to the film.

Reflectance based thermometry is a non-contact temporal technique and can achieve very high time resolution with usage of lasers of picosecond timescales. The output laser is split into ‘pump’ and ‘probe’ beams that are irradiated on the surface of sample. Due to the extremely small time scales involved, this can achieve space (depth) resolution in the range of few nanometers. This is widely used in measuring the thermal conductivity and interfacial thermal resistance of thin films [47-49]. However, the apparatus for this technique is extremely complex since this demands beam splitting of the laser, frequency modulation of the pump beam, lock-in amplifier etc. Schematic of typical setup needed for $3$-omega and Time Domain Thermo-Reflectance (TDTR) methods is shown in Figure 1.5. Scanning Thermal Microscopy (SThM), which is operated by scanning the sample surface with a sharp tip to sense the temperature, is also a popular technique that has been successfully used in understanding thermal transport in nanoscale structures [50, 51]. However, there is a need for a simple and robust technique to thermally characterize the thin films that also explores the size effect in thermal domain to
benefit experimentally. This provides the motivation for this research. In our recent work [43], we explained the heat transfer from solids to surrounding air at micro and nano scales. This technique which is based on Infrared Thermometry for thermal mapping can be extended to measure the thermal conductivity of materials.

Figure 1.5 Schematic of (a) 3 omega thermal conductivity measurement apparatus [52] (Reproduced from [52] with permission of the Royal Society of Chemistry) (b) Time Domain Thermo-Reflectance (TDTR) system [53] (Reproduced with permission)
In this dissertation, we develop and present a methodology to measure the thermal conductivity of materials with low dielectric constant (low-k). These are used as the Inter Layer Dielectrics (ILD) in microprocessor chips and their dielectric constant is lowered by varying the porosity. The results show the variation of thermal conductivity with porosity and density and is observed to follow the trend consistent with existing models. We also demonstrate an experimental set-up to measure the Interfacial Thermal Resistance between dissimilar materials. A unique sample geometry has been developed to explore the size effect of heat conduction in thin films. Infrared Thermometry is used where the surface temperature is mapped by detecting the radiance from the target material. The fabrication scheme developed for the sample ensure they are freestanding without any substrate underneath and are thermally excited from one-end in such a manner that the heat conduction is in-plane along the length of the sample. A freestanding specimen facilitates the temperature measurement since it amplifies the magnitude of interfacial temperature drop owing to the inverse proportionality of thermal resistance to the cross-sectional area. It will also help avoid the substrate effects discussed above where the penetration depth goes beyond the film thickness for very thin films. Results are presented for interfaces between metal-dielectric films, semiconductor-dielectric films and are observed to be in close accordance with those in current literature.

1.4. Multi-domain Coupling at Small Length Scales

As discussed in Section 1.1, new physics emerge and result in unusual behavior of materials at small length scales. This size effect is understood to be due to the changes in physical dimension (such as thickness), microstructure (such as grain size) [54] and their confinement effects on atomic configuration and energy distribution at smaller length scales. Law et al [55] reported that characteristic length of various physical phenomenon for solids at room temperature like electron
mean free path, phonon free mean path, the Fermi wavelength, the Debye length etc. all fall in the range of 1-100 nm and is depicted in the Figure 1.6. When the length scales of the sample specimen approach or lie in this range, there is an enhanced coupling between two or more physical domains. Existing works in the literature show the effect of mechanical strain, may be substrate induced or externally applied, on properties like thermal conductivity and electrical resistivity [28, 56-58]. With the advent of two-dimensional materials most of the studies in the past few years focused on their exceptional physical properties arising from single layer confinement. The ability to sustain very high values of strain opens up a possibility to tune their physical properties and resulted in emergence of ‘straintronics’ [59, 60]. Strain engineering is a widely used technique to achieve desirable properties and is not just limited to two-dimensional materials but also in other nanostructures [61]. It is essential to understand this correlation for a reliable design of nanoscale systems with their applicability increasing every day.

Figure 1.6 Characteristic lengths of condensed systems at 300 K [55]
Similar to the electronic properties, thermal conductivity of nanoscale solids can also be tuned with application of strain. Tensile strains as small as 6% is known to reduce the thermal conductivity by 50% in Bismuth Telluride thin films [62]. Reduction in thermal conductivity with tensile strain is also observed in graphene sheets and nanoribbons [63]. The softening of phonon modes elucidates the reduction in graphene. Figure 1.7 shows the results obtained using MD simulations. However, severe challenges like resolving and quantifying strain exist for experimental characterization of strain influence on thermal conductivity.

Transmission Electron Microscopy (TEM) is a powerful tool to visualize microstructural changes and deformation mechanism in a material upon application of strain. Application of strain in-situ TEM gives a first-hand knowledge of the associated microstructural changes that can explain the corresponding change in other physical properties. However, the main challenge lies in quantifying the in-situ experimental conditions given the chamber can only accommodate...
a 3mm diameter specimen holder grid. Chapter 4 highlights the effect of strain on thermal conductivity of Zirconium thin films. A MEMS device with integrated heaters and thermal actuators is used to heat and strain the sample respectively. The device also has strain and stress sensors which help in quantifying the respective parameters using digital image correlation technique on multiple images grabbed at different strains. TEM results demonstrate the changes in grain structure that explain the corresponding variation in thermal conductivity with strain.

1.5. Applications of Multi-domain Coupling – Thermoelectrics:

Thermoelectric technology exploits macroscopic multi-domain coupling to conversion of heat energy to electric voltage. The underlying working principle in this technology is described by Seebeck effect which states that the temperature gradient drives the diffusion of charge carriers resulting in a voltage difference. Thermoelectric Energy Conversion (TEC) devices generate power with no moving parts, zero emissions and no operating maintenance. These factors make them reliable and captivating owing to its clean energy production. However, these devices perform with a low thermodynamic efficiency. The efficiency of a thermoelectric material is determined by the figure of merit, $ZT$, a dimensionless entity defined by

$$ZT = \frac{S^2 \sigma}{\kappa} T$$  \hspace{1cm} (1.7)

where $S$ is the Seebeck coefficient, that creates a voltage difference $V (= S \Delta T)$ across the ends with a temperature difference $\Delta T (= T_h - T_c)$, $T_h$ and $T_c$ being the temperatures of hot end and cold
end respectively, $\sigma$ is the electrical conductivity, $\kappa$ is the thermal conductivity and $T$ is the temperature. The efficiency $\eta$ is related to $ZT$ as

$$\eta = \frac{\Delta T \sqrt{1 + ZT} - 1}{T_h \sqrt{1 + ZT + \frac{T_c}{T_h}}} \quad (1.8)$$

In order to maximize $ZT$, it is desired to have a high $S$ to create a large voltage per unit temperature difference, large $\sigma$ to minimize losses due to Joule heating and small $\kappa$ to maintain a larger temperature gradient. These three quantities are inter-related and lots of research has been under progress to develop materials with higher $ZT$, especially at nanoscale [65, 66]. Interestingly, existing efforts in the literature have been limited to nanostructures bulk and thin film materials to depress thermal conductivity [67-70]. This leaves a tremendous opportunity to not only enhance thermoelectric device performance by miniaturization of the device, but also explore novel in-plane designs compared to stereotyped cross-plane ones. This does not increase $ZT$, but for existing materials, it increases the efficiency and power output density while eliminating the need for heatsinks of forced convection cooling.

Current art in the commercially available TEC devices is to use thermoelectric elements with a cross-section 1.5 X 1.5 mm$^2$ and 5-10 mm high as shown in Figure 1.8a. Because of their small height, the conventional TEC devices produce a very small temperature drop without an auxiliary cooling mechanism and hence operate with very low efficiency. We propose a novel design to address this shortcoming. Chapter 5 illustrates our thin film based Thermoelectric Energy Conversion (TEC) device. This design will exploit the size dependence of heat transport in solids.
Figure 1.8 (a) Schematic of a conventional Thermoelectric Generator (TEG) using semiconductor materials with different charge carriers (b) Schematic of proposed thin film based TEG device design.

Utilizing micron-scale freestanding films of thermoelectric material produces a high thermal resistance to the heat conduction thereby resulting in a higher temperature differential as compared to bulk scale materials. The schematic in Figure 1.8b shows freestanding thin/thick films that resemble a hanging bridge structure. It is well known that a ‘bridge ices before the road’ because the bridge has both the top and bottom surfaces exposed to air, losing more heat than the road does. This is even further enhanced by using micro and nano scale thermoelectric films.

(i) The freestanding thin/thick film structures have higher heat transfer coefficient, ‘h’ for cooling in quiescent ambience. For a bulk scale or a conventional TEG, h is around 10 W m\(^{-2}\) K\(^{-1}\). In comparison, we measure it to be a few orders of magnitude higher (as high as 4000 W/m\(^2\)K) for an element of 20 x10 micron\(^2\) cross section [43].
(ii) The freestanding thin/thick film structures have higher thermal resistance. Denoted by $R_{th}$, thermal resistance is given by $R_{th} = x/(A \kappa)$, where $x$ is the length of the thermoelectric element (along the path of heat flow), $\kappa$ is the thermal conductivity of the material and $A$ is the cross-sectional area (perpendicular to the path of heat flow). For example, a 5 mm long bismuth telluride bar with 1.5x1.5 mm$^2$ cross section has thermal resistance of 1100 °K/W, while 100 x 100 micron$^2$ cross-section will yield 250000 °K/W.

The cumulative effect of these two factors result in a very large temperature drop ($\Delta T$) in thermoelectric thin/thick films. This design enables getting away with forced cooling of the cold end to maintain the temperature differential as practiced in conventional TEC devices. This device targets recovery of waste heat from industrial and residential sectors. Also, using the traditional nanofabrication process to build this device makes it highly scalable.
2. Thermal Transport in Nanoscale Low-k Inter Layer Dielectric (ILD) Materials


Author of this dissertation prepared the experimental setup, performed thin film fabrication, experiment, assisted in data analysis and corresponding manuscript writing. Tarek Alam designed the experiment, assisted in performing the experiment and data analysis and prepared the manuscript. J Bielefeld and Sean King performed the synthesis of Low-k dielectric films and assisted in manuscript preparation. Aman Haque took part in experiment design, data analysis and manuscript writing.

2.1. Introduction

Low dielectric constant (i.e. low-k) materials are used as insulating inter-layer dielectrics separating conducting metallic components such as copper damascene interconnect structures. Scaling down of transistors works against the interconnector speed due to increase in the resistance-capacitance (RC) delay. Use of Copper as the interconnect materials is already in effect to lower the resistance. Utilizing the low-k materials lowers the line-line and layer-layer capacitance and thereby reduces parasitic RC delay times enabling faster communication. However, these materials are found to have very poor thermo-mechanical properties because defects (such as small pores) are intentionally added to lower the dielectric constants. Low thermal conductivity reduces the spreading and removal rate of Joule heating produced in interconnects, which adversely impacts thermal management. Methods involving the 3ω technique [71-73] and thermoreflectance phenomenon [74, 75] have been widely used to predict data relating to thermal properties of the thin films and its variation with parameters like composition and density. The common insulating material utilized in the industry is plasma
enhanced chemically vapor deposited (PECVD) silicon dioxide (SiO$_2$) whose dielectric constant is 3.9. The incorporation of various doping agents such as fluorine [76], carbon [77] and hydrogen during PECVD are used to produce hybrid SiO$_2$ network insulating materials with reduced dielectric constant. Several organic hybrid dielectrics are also in application where spin-on deposition of the resin is utilized [76]. In the silica based dielectric materials, replacing the Si-O bond with less polar Si-C or Si-F bonds reduces the polarity and thereby lowers the dielectric constant. Also, the introduction of carbon or fluorine atoms increases the free volume in the silica structure thereby reducing the density of the material that contributes in further reduction of dielectric constant. Cross-section image of a processor with interconnects and low-k materials can be seen in Figure 2.1.

![Cross-section image of a processor with interconnects and low-k materials](http://blog.orgonlive.com)

**Figure 2.1** Cross-section of a chip from Intel showing the interconnections
For disordered or amorphous materials, theoretical models exist that predict the thermal conductivity of the material [78, 79]. Likewise, experimental methods have been developed to measure the thermal conductivity of such low-\(k\) dielectrics. Chen et al. developed a model based on effective thermal conductivity [80] to measure the thermal conductivity of low-\(k\) dielectrics and also verified the accuracy of the model using finite element simulation [76]. Standard techniques like 3-\(\omega\) [81] and thermo reflectance method [82, 83] with adjustments were found to produce quite accurate data for these materials. Kuwahara et al. [83] used the nanosecond thermo reflectance measurement system (Nano-TheMS) to measure the thermal conductivity with varying methyl content and found that it decreased with increasing methyl group content. Increased phonon scattering was proposed as the cause for the observed decrease in thermal conductivity. The temperature dependence was found to be not remarkable but a gradual increasing trend was observed. They also demonstrated that the Nano-TheMS method can be used to measure the thermal conductivity of a low-\(k\) thin film directly on a silicon substrate [82].

The porosity of the material highly affects its thermal conductivity especially at the nanoscale since it greatly influences the phonon transport. The effect of porosity on thermal conductivity was investigated and was found to decrease with increasing porosity. The effect of porosity on thermal conductivity of Xerogel films was studied by Hu et al [84] and observed the same trend. They also developed two empirical models to relate the porosity dependence of the thermal conductivity.

The thermal parameters affecting the heat conduction of a PECVD SiOC:H low-\(k\) film were studied by Sato et al [85]. They found that the low thermal conductivity was mainly a result of low thermal diffusivity attributed to discontinuities in the network structure. They also estimated the interfacial thermal resistance between the film and substrate and found a negative interfacial
resistance in the SiOC:H film. X-ray reflectivity measurements revealed a thin layer of high density at the interface which resulted in the apparent negative interfacial resistance. Hybrid organic-inorganic films like hydrogensilsesquioxane (HSQ) and methyl-silsesquioxane (MSQ) deposited by spin on deposition methods are also of interest as low-\( k \) dielectric materials. Morikawa et al [86] has used the temperature wave analysis method to determine the thermal diffusivity of such spin-on low-\( k \) dielectric thin films. They also studied the temperature dependence of these properties and observed that the thermal diffusivity decreased while thermal conductivity increased with temperature. It was proposed that the microstructural evolution during the curing process dominates the thermal diffusivity.

All the above stated methods for measuring thermal diffusivity and conductivity require the use of complex circuitry like various controllers, lock-in amplifier as well as careful optimization of experimental parameters to produce repeatable and reliable results. The objective of this study is to present a robust and simple technique to measure the thermal conductivity of low-\( k \) dielectric thin films. In our previous work, a simple technique based on temperature mapping of the sample under an Infrared Microscope (Infrascope II from Quantum Focus) to estimate the natural convection heat transfer coefficient [43] was discussed. A similar technique is applied to low-\( k \) dielectric thin films and obtained results that are consistent with the existing literature. In this article, the effect of porosity and density on the thermal conductivity of low-\( k \) PECVD carbon doped oxide (CDO - SiOC:H) and SiC:H films is studied using a temperature mapping approach and micro-fabricated freestanding cantilever beams.
2.2. Experimental Technique

2.2.1. Sample preparation

The low-\textit{k} CDO and SiC:H thin films were deposited on 300 mm diameter Si (100) wafers using industry standard high volume manufacturing plasma-enhanced chemical vapor deposition (PECVD) tools with alkoxy silane or organosilane precursors diluted in helium and various oxidizing gases (O\textsubscript{2}, CO\textsubscript{2} etc.) at 250-400\textdegree{}C [87-89]. Films with varying density and porosity were obtained by controlling the amount of a second phase organic pore builder (i.e. porogen) incorporated in the film during deposition and removed post deposition using either an electron beam or UV cure [89-91]. Table 2.1 below summarizes some of the key material properties for these low-\textit{k} films including thickness, dielectric constant, mass density, porosity, nano-indentation Young’s modulus and hardness. Details of the measurements have been described elsewhere [91-94].

Table 2.1 Material properties for low-k dielectric films investigated in this study

<table>
<thead>
<tr>
<th>Film type</th>
<th>Thickness (±2 nm)</th>
<th>Dielectric Constant, “\textit{k} (±0.1)</th>
<th>Mass Density (±0.1 g/cm\textsuperscript{3})</th>
<th>Porosity (±2%)</th>
<th>Young’s Modulus (±0.5 GPa)</th>
<th>Hardness (±0.5 GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiOC:H</td>
<td>489.2</td>
<td>3.3</td>
<td>1.3</td>
<td>8</td>
<td>5.6</td>
<td>0.9</td>
</tr>
<tr>
<td>SiOC:H</td>
<td>507.9</td>
<td>2.5</td>
<td>1.25</td>
<td>24</td>
<td>6.8</td>
<td>1.15</td>
</tr>
<tr>
<td>SiOC:H</td>
<td>504.2</td>
<td>2.3</td>
<td>1.1</td>
<td>33</td>
<td>4.7</td>
<td>0.7</td>
</tr>
<tr>
<td>SiOC:H</td>
<td>498.1</td>
<td>2.4</td>
<td>1.2</td>
<td>32</td>
<td>5.4</td>
<td>0.9</td>
</tr>
<tr>
<td>SiOC:H</td>
<td>501.9</td>
<td>2.45</td>
<td>1.2</td>
<td>27</td>
<td>6.3</td>
<td>1.0</td>
</tr>
<tr>
<td>SiOC:H</td>
<td>451.4</td>
<td>2.25</td>
<td>1.25</td>
<td>33.5</td>
<td>5.3</td>
<td>0.8</td>
</tr>
<tr>
<td>SiC:H</td>
<td>348.4</td>
<td>4.4</td>
<td>1.35</td>
<td>0</td>
<td>19.05</td>
<td>3.2</td>
</tr>
<tr>
<td>SiC:H</td>
<td>303.9</td>
<td>3.1</td>
<td>1.2</td>
<td>5</td>
<td>5.2</td>
<td>0.7</td>
</tr>
<tr>
<td>SiC:H</td>
<td>306.0</td>
<td>2.8</td>
<td>1.25</td>
<td>10</td>
<td>5.1</td>
<td>0.4</td>
</tr>
<tr>
<td>SiC:H</td>
<td>474.3</td>
<td>2.7</td>
<td>1.15</td>
<td>13</td>
<td>4.15</td>
<td>0.35</td>
</tr>
<tr>
<td>SiC:H</td>
<td>360.5</td>
<td>2.7</td>
<td>1.2</td>
<td>12</td>
<td>3.2</td>
<td>0.3</td>
</tr>
</tbody>
</table>
After the deposition of low-\(k\) films on top of the silicon wafer, samples of desired shape were made by using micro fabrication processes. Figure 2.2 shows the steps required for making the freestanding samples in rectangular shaped beams with both ends clamped.

![Fabrication process diagram](image)

Figure 2.2 (a) Schematic diagram showing fabrication process of the specimen, (b) Optical microscope image of freestanding specimen

First, photoresist is spun on the dielectric film on silicon wafer. Clamped beam pattern is translated on to the photoresist with the help of standard photolithography process (UV light exposure and development). By using the photoresist pattern as an etch mask, the low-\(k\) dielectric is removed in exposed places by reactive ion etching (RIE) process using a CF\(_4\) and O\(_2\) chemistry. The photoresist is then stripped in a solvent (Remover PG) to obtain a clamped beam shaped low-\(k\) sample with the silicon substrate exposed. Finally, the silicon beneath the sample is removed by a SF\(_6\) based isotropic deep reactive ion etching (DRIE) technique. This step is done to make the samples as freestanding rectangular beams with both ends clamped. The sample is inspected in a scanning electron microscope (SEM) to ensure that the isotropic etching of silicon
is complete and the specimen is completely released from the silicon substrate. Freestanding beams thus obtained are about 300 micron long and 5 micron wide.

Once the freestanding specimen is obtained, the specimen is transferred to a piece of thermal release tape with glue on both sides, as shown in the Figure 2.3. A small piece of thermal release tape (TRT) is placed on top of the specimen so that approximately half of the specimen length is covered by the tape. The alignment process is carried out by a three-axis micro-manipulator under an optical microscope. Then the tape is pressed gently with a plastic tweezer to ensure that the specimen is attached firmly. The tape is then peeled off swiftly, causing the beams to separate from the silicon substrate. This step results in cantilever shaped specimens on top of the thermal release tape. Lastly, the tape with specimens facing up is placed on top of a glass slide.

![Figure 2.3 Schematic diagram showing step by step specimen transfer process](image-url)
The advantages of such specimen preparation are: (i) freestanding specimens can be obtained with no substrate underneath, which makes the modeling simpler and (ii) multiple specimens can be fabricated in one device (Figure 2.3) and can be tested simultaneously. The whole sample preparation process including the development of fabrication process, specimen transfer scheme takes approximately 2.5-3 months.

2.2.2. Experimental Procedure

A typical experiment starts with placing a commercially available resistance temperature detector (RTD) on tape to the vicinity of cantilever like specimen, schematically shown in Figure 2.4b. The RTD is used as a heating element and can be aligned easily with a micro manipulator. As current is passed through the RTD it heats up the tape and base of the cantilever specimen. Due to the low thermal conductivity of the carbon doped oxide, a temperature gradient can be found in the freestanding part of the cantilever specimen. During heating of the sample with RTD, the temperature is maintained below the releasing temperature of thermal release tape, i.e. 120°C in our case.

An Infrascope II thermal microscope (Quantum Focus Instruments Corporation) is used to spatially map the temperature of the specimen. The liquid nitrogen-cooled Indium-Antimonide infrared focal plane array detector in the microscope head measures the radiance from target objects to calculate the temperature. The spatial and temperature resolutions of this infrared microscope are 2 μm and 0.1° K respectively. Figure 2.4c shows a typical temperature distribution micrograph of specimen that is obtained from the infrared microscope with input current of 35 mA to the RTD.
Figure 2.4 (a) SEM image of cantilever specimen on thermal release tape (TRT) (b) FEM simulation showing temperature gradient in the specimen due to heating of the RTD, (c) Actual temperature distribution in the sample measured by Infrared microscope

2.2.3. Mathematical model and Calibration

Mathematical model for thermal conductivity measurement of the specimen is developed through energy balance in a rectangular fin structure [95]. The energy conservation principle is applied to a specimen element that has different modes of heat flow.

\[ \frac{\partial E_{CV}}{\partial t} = \dot{E}_{in} - \dot{E}_{out} + \dot{E}_{gen} \]  

(2.1)
Since there is no internal heat generation ($\dot{E}_{\text{gen}}$) in the specimen, at steady state, heat incoming ($\dot{E}_{\text{in}}$) to a control volume is balanced by the outgoing heat ($\dot{E}_{\text{out}}$) in form of conduction, convection and radiation. The heat loss, $\Delta q_{\text{out}}$, by convection and radiation can be written as

$$\Delta q_{\text{out}} = h \Delta S (T - T_\infty) + \varepsilon \sigma \Delta S (T^4 - T_\infty^4) \tag{2.2}$$

Where $h$ is the heat transfer coefficient, $T_\infty$ is the ambient temperature, $\varepsilon$ is the emissivity of air, $\sigma$ is Stefan–Boltzmann constant and $\Delta S$ is the surface area of the differential control volume of length $\Delta x$. For small temperature differences, Equation 2.2 can be approximated as

$$\Delta q_{\text{out}} = (h + \varepsilon \sigma 4T_\infty^3) \Delta S (T - T_\infty) \tag{2.3}$$

$$\Delta q_{\text{out}} = (h_{\text{approx}}) P \Delta x (T - T_\infty) \tag{2.4}$$
P is the perimeter of the specimen cross-section. Employing Fourier’s law for conductive heat flux and Equation 2.4 for approximated heat losses by convection and radiation, Equation 2.1 is reduced to

\[ \kappa A \frac{d^2T}{dx^2} \Delta x - h_{\text{approx}} P \Delta x (T - T_\infty) = 0 \]  

(2.5)

The differential equation can be further simplified as

\[ \frac{d^2\theta}{dx^2} - m^2 \theta = 0 \]  

(2.6)

Where \( m^2 = \frac{h_{\text{approx}} P}{\kappa A} \) and \( \theta = (T - T_\infty) \). The solution to this second order differential equation can be given by

\[ T(x) - T_\infty = C_1 \sinh(mx) + C_2 \cosh(mx) \]  

(2.7)

The integration constants \( C_1 \) and \( C_2 \) can be found from boundary conditions, \( T|x=0 = T_W \) and \( \frac{dT}{dx}|_{x=L} = 0 \) (Newtonian cooling for small area). By defining sample length such that \( \frac{dT}{dx} = 0 \) at \( x = L \) (no heat input by heat conduction) and solving for the boundary conditions, we get \( C_2 = (T_W - T_\infty) \) and \( C_1 = -C_2 \tanh(mL) \). Substituting constants in equation 2.7 and rearranging gives the temperature distribution as,

\[ T(x) = T_\infty + (T_W - T_\infty) * \frac{\cosh(m(L-x))}{\cosh(mL)} \]  

(2.8)

The same solution can also be employed for the case with fixed temperature boundary conditions when the sample is held at constant temperature at both the ends. In that scenario, the total length
of sample becomes L. Evaluating constants for that results in the temperature distribution given by

\[ T(x) = T_\infty + (T_w - T_\infty) \times \left[ \frac{(T_L - T_\infty) \sinh(mx) + \sinh(m(L-x))}{\sinh(mL)} \right] \]  \hspace{1cm} (2.9)

Using the temperature data from infrared microscope, T(x) and T_w can be accurately measured as shown by the representative temperature profile in Figure 2.5b. Equation 2.8 therefore facilitates us to plot the modeled T(x) as function of thermal conductivity with the measured T(x). The measurement of heat transfer coefficient is also required to obtain the model prediction of the temperature distribution. This is already described in detail in our previous work \[43\] and is summarized below.

An exponential distribution in space surrounding a hot solid is suggested as the best fitting function by Roldan et al. \[96\] to allow T (air temperature at position y) to approach the room temperature T_\infty as y→\infty.

\[ T = T_\infty + [T_w - T_\infty] e^{-sy} \]  \hspace{1cm} (2.10)

Where T_w is the wall temperature of the specimen at the interface with surrounding air and s is a constant determined by plotting the logarithm of the temperature against the distance (y) from the specimen surface at temperature T_w.

\[ \ln \frac{T-T_\infty}{T_w-T_\infty} = s \times y \]  \hspace{1cm} (2.11)
The boundary condition that the air just adjacent to the surface is at rest and conducts heat by pure diffusion relates the temperature to the thermal conductivity of the air. The conductive heat flux \( Q \) given by the Fourier’s law of conduction is

\[
Q = -\kappa_{\text{air}} \frac{dT}{dy} \bigg|_{\text{surface}}
\]  

(2.12)

where \( \kappa_{\text{air}} \) is the thermal conductivity of air. The local heat transfer coefficient is defined as

\[
h = \frac{Q}{(T_w - T_\infty)}
\]  

(2.13)

On substituting the conductive flux at the surface, we obtain the expression for the local heat transfer coefficient as

\[
h = k_{\text{air}} \ast s
\]  

(2.14)

For calibration of this mathematical model, some samples from 400 nm thick thermally grown silicon dioxide film having similar length and width of the low-k dielectric specimens are prepared. To obtain the thermal conductivity of silicon dioxide sample, one needs to evaluate the value to constants \( s \) and \( h \), as discussed by Equations 2.11 and 2.14. Temperature profile of the RTD heater for a certain current is measured by the infrared microscope and such profile along a line is shown in Figure 2.6a. By using Equation 2.11, constant \( s \) is determined from the slope of straight line fit of the data in Figure 2.6b. The corresponding heat transfer coefficient \((h)\) is calculated as 115.06 W/m²K from Equation 2.14, where thermal conductivity of air is taken as 0.024 W/m-K. Now Equation 2.8 can be used to model the temperature profile along the oxide specimen. Experimental temperature distribution in the specimen (in the a-a’ direction) is plotted along with the modeled temperature distribution for a trial thermal conductivity of specimen in
Figure 2.6c. Thermal conductivity value which yields the best fit between experimental and model data is considered as measured thermal conductivity of the specimen. Figure 2.6c shows such fit for silicon dioxide specimen for a certain current in RTD heater and the thermal conductivity is found as 1.2 W/m-K which is a very good match with previously reported values in the literature [97-99].

Figure 2.6 Calibration of mathematical model (a) Temperature profile in RTD heater along the white line shown in inset (inset: infrared micrograph of the RTD), (b) Straight line fit of the measured data in the thermal boundary layer of RTD to obtain the value of s in Equation 2.10, (c) Measured temperature profile of 300nm thick silicon dioxide from experiment is matched with model prediction for a trial thermal conductivity value of 1.2 W/m-K

2.3. Experimental Results and Analysis

Once the temperature profile measurement of all the specimens is mapped spatially, we use the mathematical model described above to calculate the thermal conductivity. The same process described in Section 2.2 is followed to obtain the thermal conductivity of all the samples and
listed in Table 2.2. Figure 2.7 shows the measured temperature profile and predicted temperature profile for four different specimens with trial thermal conductivity values. All plots show a good fit between the measured and predicted data.

Figure 2.7 Plot of measured temperature and predicted temperature profile along the porous dielectric specimens for trial thermal conductivity values.

Table 2.2 Measured thermal conductivity of low-k dielectric films

<table>
<thead>
<tr>
<th>Film type</th>
<th>Thickness (nm)</th>
<th>Dielectric Constant, “k”</th>
<th>Mass Density (g/cm³)</th>
<th>Porosity (%)</th>
<th>Measured Thermal conductivity (W/mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiOC:H</td>
<td>489.2</td>
<td>3.28</td>
<td>1.29</td>
<td>8</td>
<td>0.40</td>
</tr>
<tr>
<td>SiOC:H</td>
<td>507.9</td>
<td>2.54</td>
<td>1.25</td>
<td>24</td>
<td>0.20</td>
</tr>
<tr>
<td>SiOC:H</td>
<td>504.2</td>
<td>2.31</td>
<td>1.08</td>
<td>33</td>
<td>0.08</td>
</tr>
</tbody>
</table>
Effect of porosity on the thermal conductivity of the investigate low-\( k \) materials is plotted in Figure 2.8. Many theoretical and semi-empirical models have been proposed previously to predict the thermal conductivity of porous materials [100-105]. In earlier models, such as by Loeb et. al. [100] and Russell et. al. [103], conduction and radiation are considered as the main heat transfer modes for a porous material. According to these models, a porous material can be treated as a two phase medium and the size, shape, orientation etc. of the pore can greatly influence the effective thermal conductivity of the material [104]. Simpler assumptions for thermal conductivity models include series and parallel paths of heat transfer through the solid and pore medium [102]. The parallel model represents the upper limit of possible thermal conductivity, whereas the series model predicts the lower limit of thermal conductivity in the porous medium. However, these models fail to match the experimental results for low thermal conductivity materials. Hu et. al. [101] proposed two semi-empirical models, namely porosity weighted simple medium (PWSM) and porosity weighted dilute medium (PWDM) model, by combining series and parallel models which give a better estimate of the thermal conductivity for a porous medium. The equations for the effective thermal conductivity (\( \kappa_{\text{eff}} \)) from these four models are given below [101, 102]:

Parallel model:  
\[
\kappa_{\text{eff}} = \kappa_f [\varepsilon + (1-\varepsilon) \kappa_s / \kappa_f]
\]  

(2.15)
Series model: 
\[ \kappa_{\text{eff}} = \kappa_f \left[ \frac{\kappa_s / \kappa_f}{\kappa_s + \kappa_f + 1 - \varepsilon} \right] \]  \hspace{1cm} (2.16)

PWSM model: 
\[ \kappa_{\text{eff}} = \kappa_s \left[ \frac{(1 - \varepsilon) \kappa_s + \varepsilon \kappa_f}{\kappa_s (1 - \varepsilon)} + \kappa_f \left[ \frac{\kappa_s}{\kappa_s + (1 - \varepsilon) \kappa_f} \right] \varepsilon^x \right] \]  \hspace{1cm} (2.17)

PWDM model: 
\[ \kappa_{\text{eff}} = \kappa_s \left[ \frac{2 (1 - \varepsilon) \kappa_s + (1 - 2 \varepsilon) \kappa_f}{(2 + \varepsilon) \kappa_s + (1 - \varepsilon) \kappa_f} \right] (1 - \varepsilon^x) + \kappa_f \left[ \frac{(3 - 2 \varepsilon) \kappa_s + 2 \varepsilon \kappa_f}{\kappa_s + (3 - \varepsilon) \kappa_f} \right] \varepsilon^x \]  \hspace{1cm} (2.18)

where \( \kappa_s \) is the thermal conductivity of the non-porous material (solid state, SiO\(_2\) etc.), \( \kappa_f \) is the thermal conductivity of the porous medium (fluid, air etc.), \( \varepsilon \) is the porosity and \( x \) is the fitting parameter.

In Figure 2.8, the measured thermal conductivity of the low-\( k \) samples are plotted with the models discussed above. Our results are in between the upper and lower limits predicted by parallel and series model. Semi-empirical models are fitted to our measured thermal conductivity values. For these two models thermal conductivity of non-porous material and pore (air) is taken as 0.7 and 0.0255 W/m-K respectively and fitting parameter is chosen as 0.15 for PWSM and 0.3 for PWDM. A detailed explanation regarding choice of fitting parameter can be found from the work of Hu et. al [101]. For Xerogel film Hu et. al. choose a fitting parameter of 0.49-0.51, whereas Coquil et. al. used a fitting parameter of 0.17 for highly ordered cubic and hexagonal mesoporous silica thin films [87].

Effect of density on the thermal conductivity can be predicted by a number of mathematical models. Among them, differential effective medium (DEM) theory and coherent potential (CP) theory are widely used [106, 107] and expressions of these models are given below:

\[ \kappa_{\text{DEM}} = \kappa_{\text{bulk}} \left( \frac{\rho_{\text{porous}}}{\rho_{\text{bulk}}} \right)^{1.5} \quad \text{and} \quad \kappa_{\text{CP}} = \frac{1}{2} \kappa_{\text{bulk}} \left[ 3 \left( \frac{\rho_{\text{porous}}}{\rho_{\text{bulk}}} \right) - 1 \right] \]  \hspace{1cm} (2.19)

where \( \kappa \) and \( \rho \) represents thermal conductivity and density of material respectively.
Figure 2.8 Measured thermal conductivity of low-k dielectrics compared with effective thermal conductivity predicted by theoretical and semi-empirical models

In Figure 2.9, predicted thermal conductivity values according to DEM and CP theory are plotted along with the measured thermal conductivity for sample specimens of different porosity. The results are observed to be more consistent with the Coherent Potential (CP) theory.

Figure 2.9 Thermal conductivity of low-k dielectric plotted with density
2.4. Conclusion

A novel experimental method is presented to measure thermal conductivity of porous low-k insulators. Traditional techniques are not highly suited to measure materials have such low thermal conductivity values. The main challenge was in establishing a large thermal gradient in the sample which is done by making it freestanding. High brittle nature of these samples also makes the experimental setup tough. But, the sample preparation is relatively easy and requires only a few micro fabrication steps. Thermal mapping under an infrared microscope is carried out to calculate the thermal conductivity of film. Our measured values are consistent with the previously reported values. Results show that thermal conductivity of porous low-k films varies non-linearly as a function of density and porosity.
3. Interfacial Thermal Resistance


Thermal resistance of interfaces is one of the most challenging measurands in experimental heat transfer, particularly for micro and nanoscale thin films. It is also the dominating quantity in thermal management in microelectronic and energy conversion devices. We present a novel technique that exploits the size dependence of thermal resistance in thin films to magnify the discontinuous temperature drop at the interface, which is then measured with infrared thermometry. Since thermal resistance is inversely proportional to cross-sectional area, we show that orders of magnitude amplification in interfacial temperature drop is possible by making the specimen freestanding, which facilitates the measurement. We present experimental results on metal-dielectric interfaces involving aluminum, copper, silicon di-oxide and hafnium oxide for validation of the technique and also measure for interface between silicon and low-k dielectric material using a slightly different fabrication process.

3.1. Introduction

Interfaces between dissimilar materials are ubiquitous in a wide variety of materials systems from composites and coatings to micro-electronics and micro-electro-mechanical systems. The property of the interface can be as important as the constituent materials, which is particularly true from thermal transport perspective. Thermal contact resistance has been widely studied for imperfect contact between two surfaces due to the presence of microscopic asperities characteristic of engineering surfaces [108]. Even with the perfect contact, interfaces create
impedance to thermal transport by developing a discontinuous temperature drop \( (T_{\text{drop}}) \) in presence of a heat flux \( q \) normal to the interface \([109]\). The first measured interfacial resistance was reported by Kapitza \([42]\) while working with liquid helium. It is essentially a proportionality constant that relates the differences in the densities and phonon propagation speeds in the two materials to measurable terms such as heat flux across an interface and the temperature drop associated with that interfacial region as given by below Equation

\[
R_k = \frac{T_{\text{drop}}}{q}
\]  

(3.1)

While the impact of interfacial thermal resistance on the overall thermal response of systems is acknowledged irrespective of length-scales \([110-112]\), it becomes particularly important for micro and nano scale systems. At nanoscale, the thermal transport phenomenon by phonons is altered due to effects like phonon boundary scattering, modifications in the phonon dispersion relation and quantization of phonons. For example, in the ever-shrinking modern semiconductor devices, very high power dissipation density means that thermal transport across the interface dictates the performance. Due to the difference in acoustic impedances and phonon group velocities, interfaces in these devices can block resist heat flow and cause chip overheating. Fundamental understanding of the interfacial thermal transport can be more important than the thermal conductivity of the materials that form the interface \([113]\). Similarly, large values of temperature drop impact applications like phase change memory (PCM) devices \([114]\) and thermoelectric energy conversion \([110]\).

The fundamental reason behind the thermal resistance is the interruption of phonons at the interfaces, represented by the phonon transmission coefficient which enables to estimate the heat flux across the interface. For perfect contacts, Acoustic Mismatch Model (AMM) \([115]\) and
Diffuse Mismatch Model (DMM) [116] have been used to predict the interfacial thermal resistance. The AMM assumes that phonons are governed by continuum acoustics. Thus, phonons impinging on the interface can reflect, refract and/or or mode-convert. An isotropic simplification is often made in calculating the phonon transmission probability in the AMM because phonons are affected by the mode of propagation (longitudinal or transverse), the angle of incidence, and the level of anisotropy in each material. The AMM has proven to be successful at low temperatures while the DMM, which assumes that the phonon loses all the previous memory upon scattering, predicts relatively well at higher temperatures. Nevertheless at much higher temperatures (~300K), around which the microelectronic devices operate, it typically underestimates when compared to the experimentally obtained values. The underlying assumption of elastic scattering in AMM gives an overestimated value of the interfacial resistance [117]. These models envisage only the phononic contribution to the heat transfer and ignore the heat transport by electrons. Therefore, interfaces involving metals as one of the materials do not give accurate results with these models.

Measurement of interfacial thermal resistance is an extremely challenging because of the small magnitude of temperature drop. Typically, the interface is structurally supported by a thick substrate that acts as a large heat sink. For films with thickness lesser than the penetration depth of the thermal waves, the film conductance cannot be isolated from the interface conductance. This offers a lower limit to the film thickness for measurement of interfacial conductance [118]. Thermally interrogating the interface without the influence of the substrate is very difficult for thin films, and basic requirement becomes ultra-fast probing [119] to minimize the substrate effects. The 3-o technique can measure interfacial thermal resistance [120, 121], but the stringent need for high frequency AC heating scales unfavorably with thermal penetration depth
to match film thickness. A much faster technique, the transient thermo-reflectance [122], is therefore more commonly used. This involves a ‘pump’ and a ‘probe’ light pulse to excite the electrons and sense the change in reflectivity with temperature respectively. This method is applicable to different materials spanning wide range of lengths, thermal conductivity and geometry [123-125]. The basic principle has been the same i.e. parametric variation of the thermal property to obtain the best fit of the model prediction to the experimental data. It is important to note that the technique not only involves sophisticated setup with a high-precision and ultrafast laser system, lock-in amplifier, polarizing filter etc., but also substantial modeling efforts even after numerous advancements to the data analysis [126-128].

The significance of interfacial thermal resistance for nanoscale thin films and heterostructures and challenges in its measurement motivate us to develop a simpler technique. The basic concept behind the novel technique is shown in Figure 3.1, where the thin films as well as their interface are nanofabricated and released from the substrate. One end of the freestanding specimen is then heated with a micro-heater to impose controlled thermal boundary condition. The remarkable feature of this setup is the fact that in absence of a substrate, the nanoscale specimen has ultra-high thermal resistance \( R_{th} \), which is given by,

\[
R_{th} = \frac{T_{hot} - T_{cold}}{q_{cond}} = \frac{x}{A\kappa} 
\]

Where, \( T_{hot}, T_{cold}, q_{cond}, x, \kappa \) and \( A \) are hot end temperature, cold end temperature, conductive heat transfer rate, length, thermal conductivity and cross-sectional area of the specimen respectively.
For example, 50 microns long, 5 microns wide and 50 nm thick aluminum specimen has thermal resistance of $1.4 \times 10^6$ K/W. We propose that such large thermal resistance causes very large temperature drop along the specimen and even more importantly at the interface, which should be easy to measure using relatively simpler techniques such as resistance thermometry or infrared techniques [129]. The heat flux can be measured from the temperature profile and the boundary conditions through energy balance, since the total heat flow into the specimen is the sum of heat flux across the interface and heat loss by convection over its surface area. Therefore, both temperature drop and heat flux can be obtained without any complicated modeling. It is interesting to note that the thermal resistance increases nonlinearly with film thickness, hence accuracy and ease of the proposed technique increases with the decrease film thickness. In contrast, the high frequency requirements for 3-ω or thermo-reflectance techniques become increasingly difficult as film thickness decreases. Also, both these techniques employ a thin metal film (10-50 nm) as the thermal heater and transducer, which may influence the accuracy for specimens with smaller or comparable thickness.

In this chapter, we present the implementation of the proposed concept using nanofabricated specimens and non-contact infrared microscopy to measure the interfacial thermal resistance between thin films of a metal and an insulator. The next section describes the fabrication processing required for the technique. The choice of a metal-insulator system is based on its prevalence in semi-conductor devices. Also, as already discussed above, the AMM and DMM fall short in accurately predicting the interfacial resistance for thermal transport across materials in which the electrons are the major heat carriers. Section 3.3 describes the mathematical model while experimental results for these interfaces are reported in Section 3.4. Finally, the conclusions are drawn on the performance of the proposed technique in Section 3.5.
3.2. Materials and Methods

In this study, we consider the specimen geometry shown in Figure 3.1. Results are presented for two kinds of interfaces: (a) Metal – dielectric and (b) Semiconductor – dielectric. The methodology for sample preparation vary slightly for the two cases and hence are discussed below separately.

(a) Metal – Dielectric Interfaces

For the interfaces between metal and dielectric films, we used 150 nm thick Copper and 100 nm Aluminum films. Two dielectric films, namely 300 nm thick silicon di-oxide and 30 nm thick hafnium oxide were used to create the Cu-SiO$_2$, Al-SiO$_2$ and Al-HfO$_2$ interfaces. All these
specimens are 10 microns wide. The length of the metal film is approximately 200 µm and 100 µm for Copper and Aluminum respectively. Figure 3.2 illustrates the nanofabrication processing steps developed for specimen preparation. Firstly, the dielectric layer is grown on a Silicon substrate, either by thermal oxidation (SiO₂) or Atomic Layer Deposition (HfO₂). The second step is to lithographically pattern cantilever type geometry on the dielectric film. The unmasked area is then etched with a reactive ion etch process containing CF₄ plasma. In the third step, another lithographic process was used to create a negative pattern of the metal film after a proper front side alignment. The metal (Copper or Aluminum) film is then grown by evaporation on to the lift-off pattern to create the aligned metal-dielectric specimen with interface. This specimen is still supported by the silicon substrate. In the fourth step, the substrate is etched using Xenon difluoride (XeF₂), which makes the sample freestanding. The heat radiation from the floor underneath can cause flawed temperature measurements of the sample. Hence, a larger depth of the floor from the sample is desired to minimize the erroneous temperature readings.

Figure 3.2. Nanofabrication processing steps to prepare freestanding metal-dielectric interfacial specimens
(b) Semiconductor – Dielectric Interface

Low dielectric constant (low-k) carbon doped oxide (CDO – SiOC:H) film is fabricated by plasma-enhanced chemical-vapor deposition on a 300mm diameter Silicon-on-Insulator (SOI) wafer. The dielectric films are made porous in the similar manner as explained in Section 2.2. Other details of this dielectric film are given in Table 3.1.

Table 3.1 Properties of the carbon doped oxide (CDO) film

<table>
<thead>
<tr>
<th>Dielectric Film</th>
<th>SiOC:H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Silicon on Insulator (SOI)</td>
</tr>
<tr>
<td>Thickness of CDO film</td>
<td>566nm</td>
</tr>
<tr>
<td>Thickness of device layer Si</td>
<td>50nm</td>
</tr>
<tr>
<td>Porosity of the CDO film</td>
<td>12%</td>
</tr>
<tr>
<td>Dielectric constant, k</td>
<td>2.6</td>
</tr>
</tbody>
</table>

It is desired to estimate the thermal resistance at the interface between CDO and device layer Silicon. The fabrication is quite distinct from the previous metal-dielectric interfaces because of the blanket CDO film grown on SOI substrate. The first step is to photo-lithographically pattern cantilever geometry on the CDO film and then etch it using a reactive ion etch (RIE) process based on CF$_4$ chemistry. Then, a rectangular beam geometry clamped at both ends and aligned with the CDO cantilever beams is patterned. The unmasked region has undergone two reactive ion etch processes to remove the device Silicon and buried oxide (BOX) layer using SF$_6$ and CF$_4$ chemistries respectively. Further a similar geometry (clamped beams) is again patterned but with a larger width than those in the previous step. An isotropic etch process using SF$_6$ makes the stacked specimen freestanding. This is then exposed to Hydrofluoric acid (HF) vapors to remove the bottom BOX layer of the stacked rectangular beam. The wider photoresist pattern in the third
step covers the lateral surface of the CDO cantilevers and ensures its protection in the HF vapor etch process. All these steps are figuratively depicted below in Figure 3.3.

Figure 3.3 Nanofabrication processing steps to prepare freestanding Silicon-CDO interfacial specimen

The patterns are designed in such a way that a series of freestanding rectangular beams are obtained after the process steps. The freestanding sample is then transferred using an ex-situ lift out (EXLO) technique on to a MEMS device with integrated heaters. The EXLO technique is based on adhesion forces and is used to manipulate specimens on to MEMS devices for in-situ testing [130]. The MEMS device used in this study has zig-zag structures heaters at both the ends of the sample and is fabricated out of SOI wafers. These structures when biased act as heat sources due to the Joule heating in them. Figure 3.4a shows the SEM image after the sample is
transferred and integrated to the device with the magnified version shown in the inset. Figure 3.4b shows thermal image of a typical device in operation to heat the sample.

![Figure 3.4](image)

Figure 3.4 (a) SEM image of the sample integrated with the MEMS device having heaters (inset: magnified image showing two sections of the sample), (b) Infrared thermal image showing the MEMS device in operation to heat a sample.

At this stage, the overlap between Silicon and CDO exists throughout the length of CDO sample. So, a physical mask is aligned on the top of sample such that it exposes only the part of sample with both CDO and Silicon. A SF$_6$ based reactive ion etch (RIE) process removes the Silicon in the exposed area. However, this is the most challenging part in the total sample preparation process due to the very small thickness of Silicon film. Even a slight over-etch can result in total sample being ruined. All these steps are shown schematically in Figure 3.5 (a), (b) & (c) and the SEM image of the final sample is shown in Figure 3.5d where only a tiny overlap exists between the Silicon and CDO film and the temperature drop is expected over this region where the heat flux crosses the interface.
Figure 3.5 (a), (b), (c) Processing steps after sample-integration with MEMS heaters, (d) SEM image showing the final sample having only a small region of overlap between Silicon and CDO films

3.3. Experimental Set-Up

Once the freestanding interfacial specimen fabrication is complete, a 2mm x 2mm resistance temperature detector (omega.com) is mounted on one side of the chip using a micro-manipulator in the case of metal-dielectric interface. This element acts as a heat source upon passing electrical current while the MEMS heaters serve the same purpose in case of semiconductor-dielectric interface. In a typical experiment, the heater element is activated with a DC current so that large, comfortably measurable temperature drop is established at the interface. The experiments are performed under an Infrascope II thermal microscope (Quantum Focus Instruments Corporation), which gives a pixel by pixel temperature map of the sample.
Figure 3.6 (a) Optical micrograph showing a freestanding specimen of interface between Aluminum and Hafnium Oxide (b) Infrared image of the specimen after activating the heater located at the metal end.

Figure 3.6 shows an optical image of the sample with interface between Aluminum and HfO$_2$ after the isotropic etch of silicon underneath. It also shows the infrared image after heating at the metal end. The infrared microscope used in this study has spatial and temperature resolutions of about 1.6 microns and 0.1 K, respectively. The sample specimen can be divided into three sections; section 1 contains the metal film alone, section 2 has an overlap between the metal and the dielectric film while section 3 is comprised of dielectric film alone. The heat carriers in the metal upon reaching start of the overlap has two paths a) travel across the interface into the dielectric and b) propagate along the metal film. Figure 3.7a shows how the region of overlap (Section 2) can be broken into elements with temperature nodes to understand the heat transport by conduction along the film and across the boundary. Figure 3.7b shows the equivalent circuit diagram drawing an analogy to an electrical circuit. $T_{m,1}$, $T_{m,2}$ and $T_{m,3}$ are the temperature nodes along the metal film while $T_{d,1}$, $T_{d,2}$ and $T_{d,3}$ are those along the dielectric film. The part of heat...
flux traveling across the interface travels past the boundary resistance \( R_k \) and shows a temperature drop from \( T_{m,1} \) to \( T_{d,1} \).

\[
\begin{array}{c|ccc|c}
\text{Metal} & T_{m,1} & T_{m,2} & T_{m,3} & \text{Dielectric} \\
\hline
T_{d,1} & T_{d,2} & T_{d,3} & \\
\end{array}
\]

Figure 3.7 (a) Schematic of the interface depicting various temperature junctions, (b) equivalent thermal resistance circuit (c) simplified version of the circuit

This is quite a complex model to quantify since it is almost impossible to obtain the temperatures of the metal and dielectric film independently in the overlap region. A simplification can be made by assuming that most of the heat flux is conducted along the metallic film in the overlap region instead of traveling across to the dielectric owing to high interfacial thermal resistance [113]. This is shown in Figure 3.7c, equivalent to saying that the heat flux goes across the interface only when it reaches the end of the metal film. Since thermal conductivity of the metal is about two orders of magnitude larger than the dielectric, this assumption does not influence the
accuracy much. This is experimentally verified in Figure 3.8, which shows that at the end of section 2, where the metal film ends abruptly, there will be a large temperature drop. Once this temperature drop ($T_{\text{drop}}$ in Equation 3.1) is measured, the interfacial thermal resistance can be calculated if the heat flux flowing across the interface is known. Our previous work [43] showed that heat transfer in rectangular patterned thin films can be modeled as a one-dimensional heat conduction problem with an extended surface. For the geometry considered in this study, the temperature distribution in a rectangular fin with a fixed temperature at the base, $T_b$, and a constant temperature $T_L$ at $x=L$, the length of the specimen, is given as

$$\frac{\Theta}{\Theta_b} = \frac{\Theta_L \sinh mx + \sinh m(L-x)}{\sinh mL} \quad (3.3)$$

where $\Theta = T - T_\infty$, $\Theta(0) = \Theta_b$, $\Theta(L) = \Theta_L$ and $m^2 = \frac{hP}{kA_c}$. $P$ is the perimeter of the specimen of constant cross-sectional area $A_c$. The method for estimation of heat transfer coefficient $h$, by approximating it with the inclusion of radiative heat transfer is described in detail by Alam et al [43]. Since the sample specimen is heated by a meso-scopic heater element for metal-dielectric interface, the heat transfer coefficient is expected to lie in the order of 100 W/m$^2$-K [131] while it is evaluated to be $\sim 3700$ W/m$^2$-K for MEMS heater in the case of semiconductor-dielectric interface.

The heat flux across the interface is obtained by evaluating the gradient of temperature distribution, given by Equation 3.3, at the tip of the metal film. Since the model prediction by Equation 3.3 is obtained at each pixel along the sample length, the gradient is obtained using the backward difference using the obtained values at the corresponding pixels. The temperature drop
(T\text{drop}) is directly obtained from the Infrared image of the specimen when heated under the microscope.

\begin{equation}
q = -k_m \frac{dT}{dx} \bigg|_{x=L}
\end{equation}

\begin{equation}
T_{\text{drop}} = T_{m,3} - T_{d,3}
\end{equation}

where \(k_m\) is the thermal conductivity of the metal thin film, \(L\) is the length to the tip of the metal film from its fixed end. Once these two quantities are known, the thermal interfacial resistance can be calculated as given by Equation 3.1.

### 3.4. Results

Figure 3.8 shows the temperature readings of the sample specimen with an interface between 100 nm Aluminum and 30 nm Hafnium oxide. The experimental values in different sections are marked in different colors. In order to verify that the heat flux be evaluated from the gradient of the temperature curve predicted by the fin model, it is also plotted in the same figure. A remarkable fit in metallic part of the sample specimen (Section 1 & Section 2) validates the approximation done in the model. The thermal conductivity values for metallic films like Aluminum (\(k = 225\) W/m-K) [57] and Copper (\(k = 250\) W/m-K) [132] are directly taken from the existing literature with similar thickness of the films. The thermal conductivity of thin films for these materials is extensively studied. For the Si/SiOC:H interface, the thermal conductivity is obtained by parametric variation to yield the best fit between the model prediction and the experimental data. This gives the thermal conductivity of silicon \(\approx 60.5\) W/m-K. The thermal conductivity of Silicon thin films is known to be much lesser than the bulk value (140 W/m-K).
and decreases with thickness due to enhance phonon scattering at the grain boundaries. The result obtained in our study is consistent with this.

Figure 3.8 Temperature distribution along the Al-HfO2 interfacial specimen

Table 3.2 Calculated values of Interfacial Thermal Resistance

<table>
<thead>
<tr>
<th>Material</th>
<th>Interfacial Thermal Resistance, $R_k$ [m²-K/W]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu on SiO₂</td>
<td>$7.74 \times 10^{-08}$</td>
</tr>
<tr>
<td>Al on SiO₂</td>
<td>$8.15 \times 10^{-08}$</td>
</tr>
<tr>
<td>Al on HfO₂</td>
<td>$3.26 \times 10^{-07}$</td>
</tr>
<tr>
<td>Si on SiOC:H</td>
<td>$5.85 \times 10^{-07}$</td>
</tr>
</tbody>
</table>

A similar procedure is followed for the interfaces between the other pairs viz. Al-SiO₂, Al-HfO₂ and Si-SiOC:H. Table 3.2 lists the computed values of interfacial thermal resistance using our technique for three different combinations of materials. Wang et al [133] computed the interfacial thermal resistance by phonon diffuse mismatch model for 1250 kinds of interfaces and
tried to give the range in which each value lies in. The values of Interfacial Thermal Resistance for Cu-SiO$_2$ and Al-SiO$_2$ are expected to lie in the order of $10^{-9}$ m$^2$-K/W as suggested in their work. The discrepancy (an order of magnitude) between our measurement and their computational prediction could arise from (i) the theory based on DMM tends to underestimate interfacial thermal resistance unless the temperature is very low and (ii) less than perfect atomic structure of the interface in this study. Zhang et al [134] studied the interfaces between metal and dielectric films using femtosecond laser transient thermoreflectance technique. They reported the thermal boundary conductance (TBC) of $0.85 \times 10^8$ W/m$^2$K ($R_k \sim 1.18 \times 10^{-8}$ m$^2$K/W) for interface between 40 nm Al and SiO$_2$. The TBC values obtained in their technique is highly sensitive to the film thermal conductivity and volumetric heat capacity as is the case with any thermoreflectance based technique. The thermal conductivity of Aluminum is heavily dependent on the film thickness which is disparate in both the studies.

Since this experiment is carried out in ambience and the sample specimens are heated further by the RTD, the sample temperatures easily go beyond 300K. At such temperatures, almost all the vibrational modes are excited and the DMM model can be expected to lower resistance compared to experimental measurements. Also the metal film was deposited on patterned dielectric that has experienced several lithographic patterning and etching processes, which may introduce contamination in the specimens. For interfaces involving metals like Aluminum, which spontaneously form native oxide (or ‘passivation’) at ambient pressures and low temperatures, the model needs incorporation of an additional resistances. A thin layer of native oxide formed gives rise to two auxiliary interfaces viz., Al-Native oxide and Native oxide- Dielectric. The measured value from the experiment is a cumulative sum of thermal resistances associated at all the interfaces. We attribute the small deviations to these above mentioned reasons. However, the
fab process for the Si-SiOC:H interface is designed such that the interface always remains intact and remains clean during the entirety of the process. The obtained value is almost an order of magnitude higher than the reported value of Interfacial thermal resistance for Si-SiO₂ interface (∼2 X 10⁻⁸ m²-K/W) [73, 135, 136]. The higher resistance at the interface can be attributed to the additional impurities and grain boundaries in the dielectric (SiOC:H) film due to the dopants and porosity present in it. Also, the small thickness of silicon films (∼50 nm) in this study when compared to large silicon substrates in the literature can contribute to further increase in the resistance.

3.4.1. Experimental Uncertainty

Evaluation of the Interfacial Thermal Resistance requires a spatial temperature map as per the methodology described. The uncertainties in length (Δx) and temperature (ΔT) measurement will introduce an uncertainty into the derived quantity i.e., the interfacial thermal resistance. The temperature and space resolution of the microscope mentioned earlier is taken as the uncertainty in temperature and length scales. Though the heat flux q at the interface is computed from derivative of temperature distribution given by Equation 3, parameters like Θ₀, Θ₇ are obtained from the infrared thermograph. Hence there is an uncertainty associated with the heat flux as well. The propagated uncertainty in the evaluation of the Interfacial Thermal Resistance, R_k, which is given by the following expression

\[
\frac{\Delta R_k}{R_k} = \frac{2\Delta T}{T_{drop}} + \frac{\Delta q}{q}
\]

Evaluating the heat flux q at the interface employs the temperature distribution given by Equation 3 and estimating the heat transfer coefficient h to obtain the parameter m. The
Experimental uncertainty associated with the heat transfer coefficient $h$, in this methodology, is described in our previous work [137].

$$\Delta q = \frac{\partial q}{\partial x} \Delta x + \frac{\partial q}{\partial \theta} \Delta \theta + \frac{\partial q}{\partial m} \Delta m$$

(3.7)

$$\frac{\Delta R_k}{R_k} = \frac{2\Delta T}{\tau_{drop}} + \frac{m(\theta_L)}{(\theta_L)' \theta_b} \sinh(mL) \Delta x + \frac{\Delta T}{\theta_b} \left[ 1 + \frac{\cosh(mL)(1 + \theta_L)}{\cosh(mL) \theta_b - 1} \right] + \frac{\Delta hP}{2mkA_c} \left[ \frac{\theta_L}{\theta_b} \sinh(mL) + \frac{\theta_L}{\theta_b} \cosh(mL) - 1 \right]$$

(3.8)

Evaluating the uncertainty in the heat flux $q$ as per Equation 3.7 and plugging it in Equation 3.6 will obtain the derived uncertainty in the Interfacial Thermal Resistance, $R_k$, as given by Equation 3.8. The corresponding values are plotted in Figure 3.9 and the uncertainty values of the physical quantities used in Equation 3.8 are tabulated in Table 3.3. These are found to lie within 10% which proves the robustness of this technique.

Figure 3.9 Uncertainty in estimation of Interfacial Thermal Resistance ($R_k$)
Table 3.3 Uncertainty values in measuring each physical parameter

<table>
<thead>
<tr>
<th>Interface</th>
<th>Δx (μm)</th>
<th>ΔT (K)</th>
<th>Δh (W/m²-K)</th>
<th>ΔRk/Rk (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al on SiO₂</td>
<td>1.6</td>
<td>0.1</td>
<td>2.66</td>
<td>6.39</td>
</tr>
<tr>
<td>Al on HfO₂</td>
<td>1.6</td>
<td>0.1</td>
<td>2.29</td>
<td>4.10</td>
</tr>
<tr>
<td>Cu on SiO₂</td>
<td>1.6</td>
<td>0.1</td>
<td>5.39</td>
<td>8.20</td>
</tr>
</tbody>
</table>

3.5. Conclusion

To conclude, we present a very simple and yet accurate technique to estimate the thermal resistance at the interface between two solids. The technique exploits the ultra-high thermal resistance of thin films when released from the substrate. We demonstrated the concept using freestanding nanoscale interfaces between metal-dielectric and semiconductor-dielectric thin films. Since the temperature drop at the interface is amplified by the absence of the substrate, conventional thermometry (infrared microscopy in this study) could be used to measure the temperature drop. The heat flux is calculated from the temperature boundary conditions after performing an energy balance in the specimen. The results obtained for standard materials are matched against the theoretical predictions by the diffuse mismatch model. The accuracy of the technique is expected to increase with decrease in film thickness (which increases thermal resistance). While this technique is based on a simple model compared to 3-ω or thermo-reflectance, specimen preparation required familiarity with nanofabrication techniques.
4. Effect of Mechanical Strain on Thermal Conductivity in Zirconium Thin Films


Author of this dissertation designed the experiment, performed the heating experiment, thermal conductivity calculations, assisted in device fabrication and corresponding manuscript writing. Baoming Wang designed the experiment, performed the TEM experiment and prepared the manuscript. Aman Haque took part in experiment design, data analysis and manuscript writing.

At the bulk scale, thermal conductivity of metals is not coupled with mechanical strain. However, this may not be the same for grain sizes below the electron mean free paths, for which mechanical deformation mechanism and volume fraction of grain boundaries are drastically different from the bulk. To investigate this hypothesis of grain size induced thermo-mechanical coupling, we developed an experimental setup to measure the thermal conductivity of 100 nm thick freestanding nanocrystalline zirconium (Zr) films as a function of externally applied mechanical strain. Experimental results show strong mechanical strain-thermal conductivity coupling, thermal conductivity of Zr film dropped from 20 W/m-K to 13 W/m-K with an increasing strain from 0 % to 1.24 %. Thermal conductivity of Zr film was also measured as a function of average grain size ranging from as-deposited 10 nm to as-grown 250 nm. The results clearly show that for grain sizes above 10 nm, mechanical strain has no influence over thermal conductivity, which supports the proposed hypothesis.
4.1. Introduction

Thermal transport in thin film components of microscale devices and systems, opto-electronics and energy conversion devices is receiving more attention because of the continuing trend in miniaturization [138-140]. Dissipative power density of these devices scales as $L^{-1}$, where $L$ is the length scale [141], which renders heat transfer in thin films critical for device performance and reliability. These devices experience varying levels of mechanical strain during their fabrication processes involving high temperatures or during device operation. Most studies typically focus on the temperature dependence of thermal or mechanical properties [142-145] and the literature lacks systematic investigation on the mechanical strain – thermal conductivity coupling. The few investigations involving mechanical deformation [146, 147] involved only intrinsic or residual strains. Also, no appreciable thermal-mechanical coupling was observed in these studies because of the large grain size. For large grains, dislocations dominate the deformation and it is well known that they scatter electrons or phonons only weakly. The advances in materials processing and computational materials science has highlighted the need for coupling effects at the smaller length-scales, where mechanical strain could possibly be coupled with thermal conductivity as a size-effect [148, 149]. Lee et al. [57] also reported strong strain influence on thermal conductivity of nanocrystalline aluminum with an average grain size of 50 nm. However, their specimens were attached to the substrate, which makes it very difficult to isolate the role of mechanical strain from the substrate accurately. A more recent study on ferroelastic Pb(Zr$_{0.3}$Ti$_{0.7}$)O$_3$ films with nanoscale domain structure showed up to 11 % change in thermal conductivity due to the electrical field assisted domain re-structuring [150]. Such active and reversible tuning of thermal conductivity shows that phonon-based transport can also be tuned by mechanical strain.
It is commonly accepted that mechanical deformation can influence thermal transport, because it affects the scattering mechanisms of thermal energy carriers (electrons and phonons). For example, electrons transfer heat in metals and are scattered by dislocations and grain boundaries. But at the bulk and micro scales where dislocation is the dominant mechanism, the thermal-mechanical coupling in metals is very weak, if any. This is because appreciable scattering of electrons by dislocations only happens at temperatures less than 100 K [151, 152]. However, thermal transport in materials is known to be size dependent at the nanoscale [153-156]. Specially, metal thin films show stronger size effect when the film thickness or grain size is smaller than or comparable to electron mean free path [157-159].

Thermal transport in pure metals contains both components of electrons and phonons. According to conventional physics, free electrons contribute to heat conduction in pure metals more than the lattice vibrations (phonons) [160]. While tacitly assumed, the question is open whether the same is true at the nanoscale. It has been reported both experimentally and theoretically that the phonon specific heat in low-dimensional system would be enhanced to a large extent [161, 162]. Heino & Ristolainen [163] computed the thermal conductivities by phonons in several metals and found they are very small compared to the experimental values due to the role of electrons. Chantrenne et al. [164] investigated the electron and phonon contributions on the thermal conductivity of aluminum films with a thickness range from 2 to 20 nm and found that it remarkably dropped below the bulk value. Feng et al. [165] studied the in-plane thermal conductivity of nanoscale copper films and concluded that even though the lattice contribution in metallic films is enhanced compared to that in bulk metal, but it is still relatively small compared to that of electrons.
The present work is motivated by the fact that the conventional physical laws break down at or below a critical length scale \([166]\), where size effects are not only shown in individual domains, but also in the coupling of these domains. As the grain size is reduced below \(~50\) nm, electrons and phonons are primarily scattered by free surfaces and grain boundaries \([167]\) instead of dislocation-based deformation mechanism which mainly takes place at the grain interior. It has been reported that ultra-fine grains are often dislocation-starved both experimentally \([168, 169]\) and theoretically \([170, 171]\). At the nanoscale, the very high volume fraction of grain boundaries (two-dimensional microstructures) plays a critical role \([172]\). As previously mentioned, the thermal conduction in nanoscale metallic films is still dominated by the role of electrons. The change of thermal conductivity because of mechanical strain must be attributed to the change of electron scattering due to mechanical deformation. The literature suggests that most of the externally applied deformation gets accommodated in grain boundaries at nanoscale \([173-175]\) as opposing to grain interiors at bulk scale, thus increasing the intensity of deformation and related carrier scattering. We hypothesize that this localization of mechanical strain results in increased defects at grain boundaries, which causes the change in thermal transport.

4.2. Experimental Setup

To investigate the effect of deformation on thermal conductivity, an experimental setup that can apply uniaxial strain on a freestanding thin film while thermal properties are being measured is required. We achieve this by designing and fabricating a micro-electro-mechanical (MEMS) tensile testing device which can be accommodated in a custom-made transmission electron microscope (TEM) holder allowing in-situ investigation. Figure 4.1a shows a SEM image of the fabricated device integrating freestanding specimen, stress and strain sensors and electro-thermal actuators. The MEMS has three pairs of electrical contact pads, A-A’ and B-B’ for heating either
end of the specimen without passing current through the specimen, C-C’ for thermal actuation, A-B’ or A’-B for passing current through specimen. The freestanding specimen is shown in Figure 4.1b at an angle of 52 degree of tilt. We chose V-shaped electro-thermal actuators for uniaxial displacement loading upon actuation.

![SEM image of the MEMS thin film tensile testing device showing its various components (b,c) schematic diagram showing displacement based force and strain measurement (d) SEM image of the heaters and the freestanding specimen](image)

Figure 4.1 Experimental Set-up (a) SEM image of the MEMS thin film tensile testing device showing its various components (b,c) schematic diagram showing displacement based force and strain measurement (d) SEM image of the heaters and the freestanding specimen

Figure 4.1c shows a schematic diagram of the device design, where the specimen is co-fabricated with a force sensor beam and a set of thermal actuator beams. These beams are micro machined from heavily doped silicon-on-insulator (SOI) wafers. By passing current through C-C’, the thermal actuator beams will expand due to Joule heating to apply load on both the specimen and the force sensing beam. The force on the specimen can be calculated from the force equilibrium diagram shown in Figure 4.1d. If the stiffness values of the force sensor and the specimen are $k_{fs}$ and $k_{sp}$ respectively, then the elongation and force in the specimen are given by [176, 177],

$$\delta_{\text{specimen}} = u_2 - u_1; \quad F_{\text{specimen}} = k_{fs} \Delta x = \left(\frac{192 k}{L_{fs}^2}\right) \Delta x$$  \hspace{1cm} (4.1)
where $\delta_1$ and $\delta_2$, are displacements in the thermal actuator and force sensing beams respectively and $\kappa$ is the in-plane flexural rigidity of the force sensing beam. These displacement values can be obtained directly from the TEM images. The maximum achievable stress and strain values depend on the stiffness of the force sensor and the specimen dimension; both of which can be controlled accurately during the fabrication process. The maximum displacement of the thermal actuator is limited to 5 microns in order to achieve high precision displacements. For a 50 micron long specimen, this results in maximum of 10% strain.

The chip shown in Figure 4.1a is fabricated using conventional nanofabrication techniques involving photolithography, reactive ion etching and evaporation of the metal film. 100 nm thick, 99.97% pure Zr thin film is first deposited on silicon on insulation (SOI) substrate using e-beam evaporator and then the device design shown in Figure 4.1a is patterned on the wafer using standard photo-lithography. Micro-heaters, force sensors and actuators are fabricated by using deep reactive ion etching (DRIE) to etch through the patterned device layer while specimen is protected by photoresist pattern. After the backside patterning, the SOI wafer is mounted on a carrier wafer using photoresist. Another DRIE process is used to etch through the backside handle layer and make the whole front-side device layer freestanding. After the backside etching is done, the SiO$_2$ layer just beneath the device layer is removed by a reactive ion etching process using CF$_4$ chemistry. Then the SOI wafer is separated from the carrier wafer using Nano PG Remover.

Finally, the silicon under the specimen (Zr film) is removed by an isotropic etch process to make the thin film freestanding while a physical shadow mask is used to protect the other parts. Figure 4.2 depicts the fabrication details. Such co-fabrication ensures perfect specimen alignment and gripping [168]. After fabrication, the device is wire bonded to make the proper electrical contacts.
and mounted on either the gold coated ceramic pads for in-situ infrared microscope measurement or on a TEM specimen holder with electrical biasing capability for in-situ TEM investigation.

Figure 4.2 Fabrication of MEMS thermo-mechanical testing device

Figure 4.3a shows the TEM bright field image and selected area diffraction pattern of the as-deposited specimen. The average grain size of the 100 nm thick films is around 10 nm. Nanocrystalline structure is also evident from the selected area diffraction pattern, which shows diffused rings representing grains with various crystallographic orientations. Grain size and thickness are two parameters that make thin film mechanical properties different from the bulk.
For example, the yield stress and fracture strain of bulk poly-crystalline Zr are about 400 MPa and 24 % respectively [178]. For 100 nm grain size and 80 microns foil thickness, these values change to 850 MPa and 2.75% respectively. To accurately characterize our 100 nm thick and 10 nm grain size specimens, we performed uniaxial tensile tests using the procedure described above. The stress-strain diagram, shown in Figure 4.3b, is remarkably linear. This suggests that dislocation based plasticity is absent due to the extreme microstructural (grain size) and dimensional (film thickness) constraints. As a result, the fracture stress is very high (about 1.2 GPa) at the expense of fracture strain (1.5 %).

Figure 4.3 Bright-field TEM image of the as-deposited specimen (b) Stress-strain diagram of the specimen

Thermal conductivity measurements were conducted under infrared (IR) microscope. Figure 4.4a shows a typical thermal mapping from the IR microscope when the electric contact pads B-B’ in Figure 4.1a are powered up. The freestanding specimen is modeled as a simple extended fin as shown in Figure 4.4b. Energy balance is applied on a control volume of the specimen with a length of $\Delta x$. 
\[
\kappa A \frac{dT}{dx} \bigg|_x - \kappa A \frac{dT}{dx} \bigg|_{x+\Delta x} = hP\Delta x(T - T_\infty)
\]  
(4.2)

where \( \kappa \) is thermal conductivity of specimen, \( A \) and \( P \) are cross-sectional area and perimeter, \( h \) is the overall heat transfer coefficient (summation of convection \( h_c \) and radiation \( h_r \)) and \( T_\infty \) is the ambient temperature. For small temperature difference, \( h \) can be expressed as [179]:

\[
h = \varepsilon \sigma 4T_{amb}^3 + h_c
\]  
(4.3)

where \( \varepsilon \) is the emissivity (0.48 [180] for Zr) and \( \sigma \) is the Stefan-Boltzmann constant (5.67\times10^{-8} \text{ W m}^{-2} \text{ K}^{-4}). The general solution of Equation 4.2 is:

\[
\theta = C_1 e^{mx} + C_2 e^{-mx}
\]  
(4.4)

where \( \theta = (T - T_\infty) \) and \( m = \sqrt{hP/\kappa A} \).

\( C_1 \) and \( C_2 \) can be obtained by applying boundaries, \( T=T_b \) at \( x=0 \) and \( T=T_L \) at \( x=L \). Then the solution can be given by:

\[
\frac{T - T_\infty}{T_b - T_\infty} = \frac{[T_L - T_\infty / T_b - T_\infty] \sinh mL + \sinh m(L-x)}{\sinh mL}
\]  
(4.5)

The calculated temperature profile \( T \) can be plotted as a function of \( \kappa \) using Equation 4.5. If heat transfer coefficient \( h_c \) is measured accurately, by matching the modeled temperature profile \( T \) with experimental data from IR microscope, thermal conductivity \( \kappa \) can be measured. Figure 4.4c shows such curve fitting of the model to match it with experimental data with \( \kappa \) as the only fitting parameter. The heat transfer coefficient \( h_c \) can be acquired by applying energy conservation principle near the heated specimen surface [181],
\[-\kappa_{\text{air}} A \frac{\partial}{\partial y} (T - T_s) \bigg|_{y=0} = h_c A (T_s - T_\infty)\]  \hspace{1cm} (4.6)

where, \(y\) is the perpendicular direction to the specimen length (\(y = 0\) denotes specimen surface) and \(T_s\) is the specimen temperature. The solution is given by,

\[T = T_\infty + (T_s - T_\infty) \ast e^{-sy}\]  \hspace{1cm} (4.7)

where \(s = \frac{h}{\kappa_{\text{air}}}\). Rearrange equation 4.7,

\[\ln \left(\frac{T-T_\infty}{T_w-T_\infty}\right) = -sy\]  \hspace{1cm} (4.8)

Here, the term \(s\) can be determined from the logarithm plot of the temperature difference ratio against distance \(y\) from the specimen surface with temperature \(T_s\) as shown in Figure 4.4d. This method has been validated using materials with known thermal conductivity [181]. With this experimental setup, the electro-thermal actuators are activated with different biases to apply different mechanical strains on the sample. The temperature profile is mapped using an Infrascope II thermal microscope (Quantum Focus Instruments Corporation), whose liquid nitrogen-cooled Indium-Antimonide infrared detector measures temperature with 0.1 K resolution. In this study, a 15x objective was used, which provides pixel to pixel resolution of about 2 microns. At each strain, the temperature profile is recorded for the calculation of thermal conductivity. The strains are measured later using optical microscope and digital image correlation technique.
4.3. Experimental Results and Analysis

Figure 4.5a shows comparison of the experimental temperature profile with model predictions at three different strains. Since the model is based on constant (not temperature dependent) thermal conductivity, the observed fit between the model and experiments reflects the negligible role of temperature dependent thermal conductivity at the relevant temperature range. The estimated thermal conductivity is also listed. In order to eliminate the effect of temperature on thermal
conductivity, the hot end temperature of the specimen is kept almost constant during all the measurements. The thermal conductivity measured at zero strain is measured to be 20 W/m-K. Due to the lack of data on the thermal conductivity of nanocrystalline Zr, we compared the measured result with the value of bulk Zr which is around 22.6 W/m-K [182, 183]. This validates our experimental procedure since the literature suggests that thermal conductivity will decrease when the grain size becomes smaller. Figure 4.5b summarizes the obtained results with a strain range from zero to 1.244 %, where the thermal conductivity clearly decreases as we increase the strain. This behavior can be ascribed to the nanocrystalline microstructure of these thin films. When the geometric dimension of specimen or the grain sizes go down to nanoscale, it becomes increasingly difficult for the grain interiors to accommodate the external deformations. For example, in aluminum, dislocations may cease to exist in grains as large as 60 nm [168, 169]. Therefore, mechanical deformation mechanisms for grain sizes smaller than about 50 nm are basically different from the bulk ones which is not only due to absence of dislocations but also very high volume fraction of the grain boundaries [166]. Absent of dislocations in the grain interior, the grain boundaries primarily accommodate the applied strain [159]. To accomplish this, the grain boundaries must slide, rotate or emit dislocations that also move along the grain boundaries as strain is applied [167]. The scattering of electrons by grain boundaries will be enhanced by these grain motions [57]. Therefore, we hypothesize that the motion of grain boundaries resulted from strain localization is the primary mechanism behind thermal-strain coupling.

This hypothesis is also supported by Coble creep deformation mechanism [184] which suggests that deformation in a material occurs through diffusion of its atoms along the grain boundaries causing a sliding motion in them. In Coble creep, the strain rate \( \dot{\epsilon} \) is proportional to \( d^{-3} \), where \( d \)
is the average grain size. As the grain size becomes smaller, this mechanism dominates the Nabarro- Herring creep mechanism [185] in which the strain rate is proportional to $d^{-2}$. In Nabarro- Herring creep, the deformation occurs through diffusion of atoms along the grain interiors i.e., the lattice. Nabarro- Herring creep deformation would not show any coupling of thermal conductivity with mechanical strain.

![Figure 4.5](image.png)

Figure 4.5 Experimental results for as-deposited specimens with 10nm grain size. (a) Comparison of experimental temperature profile with model prediction at various strains (b) Plot of measured thermal conductivity as a function of externally applied mechanical strain

To further verify our original hypothesis that mechanical deformation is coupled only in the grain size range that is comparable to (or smaller than) the electron mean free path, we repeated the experiments shown in Figure 4.5 as a function of grain size. The electron mean free path in Zr at room temperature is about 10 nm [186], which is just about the grain size of our specimens. For the as-deposited specimens, we observed remarkable thermal-mechanical coupling (Figure 4.5b). For larger grain sizes, we expect the thermal conductivity to remain constant irrespective of grain size or mechanical strain. To perform this investigation, we electrically annealed the
freestanding specimen in-situ a transmission electron microscope (TEM) by passing current through them. Figure 4.6a and 4.6b show two specimens with average grain size of 10 nm and 250 nm, respectively. Figure 4.6c shows the measured thermal conductivity (consistent value of 20 W/m-K) as function of grain size that was increased by electrical annealing. We then performed mechanical straining for these grain sizes (50, 120 and 250 nm). We did not observe any mechanical strain dependence of thermal conductivity in these specimens, which supports our hypothesis that the thermo-mechanical coupling is absent for grain sizes more than the electron mean free path.

![Figure 4.6 TEM bright-field image of (a) as-deposited specimen (b) specimen after grain growth with an average grain size of 250nm (c) Plot of thermal conductivity as a function of grain size](image)

It is known that even small amounts of impurity concentration can have a dramatic effect on the properties of nanocrystalline metals. A critical O impurity concentration is known to immobilize the grain boundaries and affects the deformation behavior. In the case of Zirconium, this can also be explained by the higher bond dissociation energy of Zr-O bond (766 kJ/mol) than Zr-Zr bond (298.2 kJ/mol) [187]. The base pressure during the deposition process of the metal governs the impurity concentration in the material. For a metal like Aluminum, the impurity (oxygen)
concentration is observed to reduce from 1.76 % to 0.18 % when the deposition base pressure is reduced from ~10^{-5} Torr to ~10^{-6} Torr [188]. Hence, it is to be ensured that the deposition process happens at lower base pressures (~ 2 X 10^{-6} Torr in this study) to observe the multi-domain coupling behavior in nanocrystalline metals.

4.4. Conclusion

In this study, we measured thermal conductivity of 100 nm thick Zr films as a function of externally applied mechanical strain. The average grain size of the specimen is about 10 nm. The results show a decrease trend of thermal conductivity with increasing strain. We propose that the increasing scattering of thermal conduction electrons is due to the deformation localization at the grain boundaries which enhances the motion of grain boundaries (or results in increased defect concentration), thus pronouncing scattering of electrons. This hypothesis is further verified by the measurement of thermal conductivity as a function of grain size, which shows a constant value of 20W/m-K at average grain size ranging from 10 nm to 250 nm. The experimental results indicate the validity of our hypothesis that mechanical strain-thermal conductivity coupling is primarily size induced and is absent when the characteristic length-scale (thickness of grain size) is greater than the electron mean free path.
5. Application of Thermal Size Effects on Waste Heat Energy Harvesting

This chapter will demonstrate a novel concept Thermoelectric Energy Conversion (TEC) device. The current state of art technology of thermoelectric generators (TEGs) involve using bulk-scale thermoelectric elements with the cold end maintained at a design temperature by various means. The design will exploit the size dependence of thermal transport in solid state materials to benefit the performance. This involves using micron-scale films of thermoelectric material manufactured using conventional microfabrication techniques, which makes it scalable too. The fabrication process and results of the TEG are shown and its application in powering the wireless sensors is also demonstrated. The geometry and design is unique in way that it gets away with the need of coolant flow or a heat sink on the cold side of TEG. Preliminary simulation results show that the Carnot efficiency close to 10% is achieved for a hot surface at temperature of 100 °C.

5.1. Introduction

Waste heat energy is found in abundance in various industrial and residential sectors ranging from manufacturing, automotive, refrigeration and other applications. Statistical investigations show that about ~50% of input energy in the industrial sector is wasted as heat in the United States. Harvesting even a fraction of this heat will have a profound impact on the energy sector and even the economy of a nation. With carbon emissions reaching all-time high and more awareness being created towards protecting our environment, greater impetus is with the alternative sources involving clean energy production. Thermoelectric technology, a solid-state energy conversion, is based on transforming the heat energy into electrical energy and vice-versa. These devices are based on Seebeck effect which states that temperature difference in a
material drives the charge carriers (electrons/holes) thereby resulting in an electric current. Peltier effect is the opposite of Seebeck effect where the flow of charge carriers generate a temperature gradient in the material. Thermoelectric devices based on Seebeck effect are typically used for power generation and those based on Peltier effect are used in active refrigeration applications. Moreover, they do not have any moving parts thereby requiring minimal maintenance and close to zero operating costs making it a viable technology for scavenging waste heat. Seebeck coefficient is a material property that is defined as the voltage $\Delta V$ created across two ends of a material having a temperature difference $\Delta T$

$$S = -\frac{\Delta V}{\Delta T} \quad (5.1)$$

However, these devices suffer from low efficiencies. The key parameter in evaluating the efficiency of a thermoelectric device is the dimensionless figure of merit, $ZT$. The expressions for both figure of merit ($ZT$) and efficiency ($\eta$) are already discussed in Section 1.5. Logically, materials with large Seebeck coefficient ($S$) and electrical conductivity ($\sigma$) and smaller thermal conductivity ($\kappa$) are the best materials for building devices with superior performances. It has also been the subject of active research for discovering novel nanostructured materials with efforts in changing the lattice structures, density of states to give a superior $ZT$ [66, 189-191].

The current state of art in commercially available Thermo-Electric Generators (TEGs) is to use thermoelectric elements of cross-section $\sim 1.5 \times 1.5 \text{ mm}^2$ and about 5-10 mm height. For such geometries, a very tiny temperature drop is achieved by natural convection which results in a small efficiency. Hence, they demand auxiliary cooling mechanisms like a heat sink and/or forced fluid cooling of the cold side to maintain a high temperature differential to achieve better efficiencies. This involves further expense of energy to maintain the cold end temperature and
also occupies extra space due to additional components. Such conventional TE units are shown in Figure 5.1 (a) & (b) while the schematic design of TEG in this work is shown in Figure 5.1c.

Figure 5.1 (a) Schematic of a conventional TE unit with heat sink [192], (b) forced cooling mechanism with a fan and (c) schematic of a cantilever resembling design of TEG in this work

Doped semiconducting elements are generally used in these commercially available modules. Bismuth Telluride is the most widely used material owing to its low thermal conductivity ($\kappa \approx 1$-2.5 W/m-K) and high Seebeck coefficient (S~200-250 $\mu$V/K). Elements with opposite polarity (n- and p-type) form one basic unit cell of a TE module as seen in Figure 5.1a. The output power $P$, for one unit cell is given by expression

$$P = \Delta T^2 S_n^2 \sigma_n \frac{A_c}{4L} + \Delta T^2 S_p^2 \sigma_p \frac{A_c}{4L} \quad (5.2)$$

where the n- and p-type legs (denoted by subscripts) have cross-sectional area $A_c$ and length $L$. These units are then repeated in series to give the desired output voltage of a TEG device. The total voltage and resistance are used in calculating the power output of the device.
5.2. Design Features

The schematic shown in Figure 5.1c depicts the uniqueness of this design where n-type and p-type element are freestanding structures. It has an extra surface exposed to air enabling it to lose more heat which is very similar to ‘bridge ices before the road’ phenomenon. This design also exploits the size effect of heat transport in solids. Using thermoelectric films with micron scale thickness will let us take advantage of two physical phenomenon which are the major highlights of this design:

(a) High Thermal Resistance

The geometry employed by using freestanding micron scale structures makes it a case of in-plane heat conduction. Thermal resistance, denoted by $R_{th}$, to heat transport by conduction in a solid is already defined earlier in Section 3.1 and is given again below

$$ R_{th} = \frac{L}{A_c \kappa} \quad (5.3) $$

where the symbols mean the same as before. Having a very small thickness and width of the thermoelectric sample limits the cross-sectional area $A_c$ to very small value thereby resulting in a high thermal resistance. For a given heat transfer rate, this results in amplification of temperature drop across the thermoelectric sample. This is analogous to a high voltage drop across a high-impedance resistor for a given current flow in it. Also, lack of a substrate directly underneath the sample promotes heat transfer by conduction within the sample. Of course, this means an additional surface for heat loss by convection to surrounding air which is discussed later in this section. Further, using a material like Bismuth Telluride which is known to have a low thermal
conductivity results in a high temperature drop which is desired for high electrical voltage output.

(b) High Heat Transfer Coefficient

The heat transfer coefficient ‘h’ is the measure of heat flux lost to the surrounding fluid per unit temperature difference between the solid surface and the surrounding fluid. The mechanism of heat transfer from hot solids to surrounding environment is well established for bulk scale free and forced convection but very little is known for solids at micron and submicron length scales. The physics of solid to gas heat transfer changes considerably at length scales that are on the same order of certain characteristic lengths [193-196].

At the macro scale, the bulk flow (either due to density variation of externally imposed) of the fluid surrounding a heated solid is primarily responsible for convective heat transfer. This is commonly known as advection. A second mode of heat transfer is through diffusion and/or conduction at the still boundary layers next to the solid. Maxwell [197] introduced the concept of molecular conduction in gases. At the bulk scale, the heat transfer coefficient is a weak function of temperature of the hot solid. The relative contribution from the two mechanisms, advection and molecular conduction, determines the nature of the temperature and pressure dependence of heat transfer coefficient.

While for macroscale objects, density difference drives the flow associated with natural convection, the buoyancy forces at smaller scales are too weak to overcome the viscous drag which opposes the convective motion. When a heated microstructure is suspended in air, the dominant mode of heat transfer is conduction through the air, and natural convection becomes less important [193, 198]. Due to the small size of system, density variations are very small in
the control volume and thus gravitational forces do not become significant. This implies that at
the microscale, the classical notion of advection may not be dominant and conduction should be
considered [199, 200]. Studies suggest that larger surface area to volume ratio in the heated solid
has an impact on the heat transfer coefficient. The general consensus is that the heat transfer
coefficient increases with decreasing length scales. The value of $h$ for bulk scale free convection
is generally within the range of 10-25 W/m$^2$K. A simple scaling argument using the correlation
between Nusselt, Rayleigh and Prandtl numbers let Peirs et al [196] suggest $h$ to lie in the order
of 100 W/m$^2$K for air at length scales around 100 µm. Several other studies reported heat transfer
coefficient values to lie in the range of 100-7000 W/m$^2$K for different cases involving microscale
heated solids. In our prior work, we have measured heat transfer coefficient to lie in the range
3000-4000 W/m$^2$K for Silicon microstructures of dimensions in the range of few tens of microns
[43] and also observed a pronounced dependence on temperature. For a bulk scale solid without
any forced fluid flow, $h$ is known to be in the span of 5-20 W/m$^2$K [95].

Figure 5.2 (a) SEM picture of silicon microstructure with a heater and specimen, (b) temperature
profile along the specimen with ‘$h$’ at each section of the specimen [43]
The combined effect of the (i) increased free convection heat loss and (ii) increased thermal resistance results in very large $\Delta T$ in the thin/thick films of thermoelectric elements. It is important to note that the electrical resistance also increases with decrease in the thermoelectric cross-sectional area. However, the effect of thermal resistance scales as a squared function. This is because power output is a squared function of the temperature difference. The effect of electrical resistance, on the other hand is linear. For example, 100 times increase in thermal resistance would positively influence 10000 times through temperature difference, while negatively influence 100 times through increase in electrical resistance, therefore then net increase in power is 100 times.

5.3. Performance Testing

Bismuth Telluride is chosen as the constituent material of the thermoelectric element consistent with the other existing commercial products. It is one of the best available thermoelectric materials owing to its favorable properties like electrical conductivity, thermal conductivity and Seebeck coefficient. Producing Bismuth Telluride by Zone melting method is known to provide with high quality ingot with an improved yield [201]. We purchased similarly manufactured Bismuth Telluride in ingot form from a commercial vendor. The measured properties of both n- and p-type procured materials are tabulated below in Table 5.1

Table 5.1 Measurement of the physical properties of procured Bismuth Telluride (ingot form)

<table>
<thead>
<tr>
<th>Material</th>
<th>Seebeck coeff.</th>
<th>Electrical resistivity</th>
<th>Thermal conductivity</th>
<th>ZT (300 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-type Bi$_2$Te$_3$</td>
<td>220 $\mu$V/K</td>
<td>8x10$^{-6}$ ohm-m</td>
<td>2-2.5 W/m-K</td>
<td>0.9</td>
</tr>
<tr>
<td>p-type Bi$_2$Te$_3$</td>
<td>180 $\mu$V/K</td>
<td>9x10$^{-6}$ ohm-m</td>
<td>2-2.5 W/m-K</td>
<td>0.55</td>
</tr>
</tbody>
</table>
Since the objective is to obtain thermoelectric films of very small thickness (around few tens of microns), the procured material is pulverized into powdered form with ~10 micron size particles using a high-energy ball mill. The powder is then mixed with a polymeric binder to prepare a thermoelectric ink. The ink was then used with a screen printer (AMI Screen Printer Model 645) after a 5 by 5 inch screen mask was created. The ink is deposited through the screen onto the substrate at a typical thickness of 25 microns and line width of 150 microns. The films were finally cured at 400 °C in a vacuum oven for 6 hours. Though the measured thermal conductivity of printed thermoelectric film (~ 0.8 W/m-K) is lower (and favorable from the performance standpoint) than the as-received ingot form, the electrical resistivity was observed to be very high. For example, a printed film that is 25 micron thick, 150 micron wide and 5 mm long showed an electrical resistance of about 100 kΩ and that high resistance will result in a low power output. It was found that when the binding agent leaves the material during curing, it leaves numerous large pores that results in poor electrical conductivity. Hence, it was decided to not pursue the printing technique anymore.

The next activity undertaken was micromachining of bismuth telluride ingots. We used diamond saw cutting and mechanical polishing tools to obtain sample films of thickness around 400 microns. It is to be noted that the material produced by zone melting method becomes very fragile and is extremely difficult to polish down to lesser thickness. Hence the width of each sample was limited (~1mm) in order to ease the handling and did not go to dimensions much lesser in magnitude (few hundreds of microns). The sample is suspended on two ends such that the length of sample i.e. distance between the ends i.e. L ~2.5 mm. It was then heated at one end using a mesoscale heater, a Room Temperature Detector (RTD) element which when powered acts as a heat source. The temperature profile along the sample is mapped using Infrared
Microscope and the corresponding thermal image is shown in Figure 5.3a. Temperature in the region surrounding a hot solid is expressed as an exponential distribution and is given by Equation 5.4. The corresponding plot is shown in Figure 5.3b using the lateral temperature scan T(y) to determine the exponent, s. Heat transfer coefficient is then calculated using Equation 5.5 where $\kappa_{\text{air}}$ is thermal conductivity of air. The temperature profile along the length of sample $T(x)$ can be modeled according to Equation 5.6 where $T_b$, $T_L$ are temperatures at base $x=0$ and length $x=L$ respectively, $T_\infty$ is the ambient temperature, $m^2 = hP/\kappa A_c$ ($P$ is the perimeter and $A_c$ is cross-sectional area of sample). The plots of temperature profile along the line trace from Infrared thermal image and the model prediction are seen in Figure 5.3c. The goodness of the best fit between the two plots is evident for the case of thermal conductivity $\kappa = 2.49$ W/m-K which concurs well with the value 2.44 W/m-K reported in literature [202].
\[
\ln \left( \frac{T(y) - T_\infty}{T_w - T_\infty} \right) = -sy
\]  
(5.4)

\[
h = \kappa_{\text{air}} s
\]  
(5.5)

\[
\frac{T(x) - T_\infty}{T_b - T_\infty} = \left[ \frac{T_L - T_\infty}{T_b - T_\infty} \right] \frac{\sinh mL}{\sinh m} + \sinh m(L-x) \frac{\sinh mL}{\sinh mL}
\]  
(5.6)

The hot end of sample is maintained approximately at 80°C upon passing 50mA DC current in the RTD element. A temperature differential of 45°C is obtained in the sample across its length and is discernible in Figure 5.3c. This large differential is predominantly due to an increased heat transfer coefficient.

Figure 5.4 (a) 3D image of the surface temperature plot from COMSOL simulation for the case with heat transfer coefficient \( h = 133 \text{ W/m}^2\text{K} \), (b) Temperature line plot along the top edge for the above geometry shown for 3 different cases to validate the hypothesis that microscale thermoelectric films give a high temperature differential predominantly due to an increased heat transfer coefficient.
For a 400 micron thick bismuth telluride film, we measure $h = 133.4 \text{ W/m}^2\text{-K}$, which is 5 times higher than the largest value cited in the literature. This validates the claim made for the higher temperature differential in the case of a freestanding thermoelectric design. In order to comparatively evaluate the individual effect of increased thermal resistance and heat transfer coefficient, a simple COMSOL simulation of heat transfer in Bismuth Telluride for different cases is done. Figure 5.4 summarizes the findings. The conventional design use thermoelectric elements with cross-section $1.5 \times 1.5 \text{mm}^2$, for this size the $h$ value is at most $20 \text{ W/m}^2\text{-K}$. For this design the temperature differential is about $\Delta T \approx 8 ^\circ \text{C}$. For our actual sample, the cross-section is $1 \times 0.4 \text{ mm}^2$, for this size the $h$ value is $133.4 \text{ W/m}^2\text{-K}$. For this case the temperature differential is about $\Delta T \approx 44 ^\circ \text{C}$ which is almost 6 times larger than the conventional design. We also show a hypothetical scenario, if the $h$ value were not $133.4 \text{ W/m}^2\text{-K}$ but only $20 \text{ W/m}^2\text{-K}$; the temperature differential is about $\Delta T \approx 15 ^\circ \text{C}$. This is exclusively due to the increased thermal resistance owing to a reduction in cross-sectional area of the sample.

**5.4. Fabrication Scheme of TEG**

**5.4.1. Assembly of micro-machined thick Bismuth Telluride samples**

Inspired by the results, a scheme for assembly of the micro-machined Bismuth Telluride samples has been developed to form a functional device with multiple thermoelectric elements with opposite polarities connected in series to form a closed electrical circuit. Use of oppositely doped elements alternatively makes it convenient to form a series by simply connecting the cold/hot ends of adjacent samples and this is depicted in Figure 5.5a. A template to aid the assembly process was designed and carved out of a thin ceramic plate by laser based machining. This intermediate step of the assembly process with the template usage is depicted in Figure 5.5b. Figure 5.5c shows the final device after assembly of 10 pairs of thermoelectric samples with each
pair consisting of an n- and p-type sample which generates an output voltage of 137 mV on a hot surface at temperature 100 °C. For the measured Seebeck coefficients as reported in Table 5.1, this implies that \( \Delta T \approx 34.5 \) K was achieved. This is approximately twice than that is achieved by existing commercial products (\( \Delta T \sim 15 \) K for hot side temperature at 100 °C). The resistance is around 3 Ohms, resulting in 6.25 mW power. The specific power i.e. power per unit area = 1 mW/cm\(^2\).

![Figure 5.5](image)

Figure 5.5 (a) Assembly schematic of the micro-machined thermoelectric samples, (b) ceramic template using for the assembly, (c) assembled device in operation on hot surface at 100 °C producing \(~137\) mV output (inset)

The results indicate that the electrical resistance is too high for the device which is the key reason for low power output. This arises from using an incompatible solder alloy (Pb/Sn alloy) that has a high contact resistance when used with Bismuth Telluride. Using several interconnects to close the circuit multiplies the number of contacts and further deteriorates the total resistance.

In order to manifest this, a single pair device (with dimensions 3 X 30 mm\(^2\)) was built with the n- and p-type samples soldered with an intimate physical contact. This avoids the need of an interconnect and hence results in a very low device resistance. This device had a resistance of 0.05 Ohms and produced 14.5 mV when the hot surface temperature was set to 100 °C. For a temperature differential of 35 K, the Carnot efficiency is 9.4%. The Carnot efficiency is the
efficiency of Carnot cycle operating between the same temperatures as that of the heat engine and is given by

\[ \eta_{\text{carnot}} = 1 - \frac{T_c}{T_h} \]  

(5.7)

To benchmark this performance, two commercially available products were procured and placed on a hot surface of 100 °C along with the single pair device. The cold side of these devices are kept uncontrolled (no air or water cooling). The voltage, resistance and size information is given below in Figure 5.6. Figure 5.6b shows infrared thermal image where the top surface temperature is measured to be around 80 °C, which indicates that temperature differential is about 20 K for the commercial products, which gives Carnot efficiency of 5.3%. We only report the Carnot efficiency, since we do not know the exact ZT value for the commercial products. The specific power obtained by our product is about 7 times higher than the nearest competitor. The Carnot efficiency is about 2 times that obtained by the commercial products.

Figure 5.6 Performance comparison of the TEGs on hot surface at 100 °C temperature and unconstrained cold side temperature (a) existing product 1 (b) infrared thermal image showing cold surface temperature for existing product 1 (b) existing product 2, (c) our product
5.5. Applications

5.5.1. Microprocessor

Modern data centers have the processors as hot as 100-120 °C, which are cooled by an airflow. This has a very large potential market for energy scavenging. We have performed preliminary studies on the developed prototype for possible heat scavenging from data center/servers. This was done at the Penn State University’s server room, on a 1U processor module, running only at 20% rated load (idling). Figure 5.7 shows a single and a 4 n-p pair thermoelectric prototype device mounted on the processor. When mounted on a processor with 80 °C surface temperature, the 1 pair prototype produced power density of 14.4 mW/cm², which is much better than the previously obtained value (4.6 mW/cm²). This is because the server room maintains active airflow for air-conditioning, whereas our previous tests were performed in quiescent air.

![Figure 5.7](image)

Figure 5.7 (a) Single pair and (b) 4-pair prototype device mounted on a server microprocessor surface
5.5.2. Wireless Sensor Networks (WSN)

The advances in wireless sensing and communication systems has paved way for the Internet of Things (IoT). It is like an extension of the current Internet representing a connection of people, process, data and things together. This has an enormous potential of new products and services in the future. It is an emerging trend and research in this area has gained momentum after it attracted collective efforts from academia and industry [203-205]. A routine wireless sensor module has several constituents composed of low-power sensing devices, electronics and wireless transceivers. The power supply to these systems should hence be miniaturized and everlasting in order to enable a maintenance-free solution. Conventional batteries do not serve this purpose. Energy harvesters that scavenge energy from various sources like light energy, kinetic energy, thermal energy and convert into electrical energy are best suited. A thermoelectric generator (TEG), which exploits the Seebeck effect, can deliver the required power output. Application of the developed prototype to power such wireless sensors is discussed in this Section. These sensors do not operate at high temperatures as before but limited to 100 F (~37°C), that is prevalent at several places in our daily lives. These sensors incorporate a step-up topology to operate with low-input voltage sources like TEG and require input voltages as low as 20mV. In order to meet the voltage requirements, we assembled multiple n-p pairs as depicted in Figure 5.8. It is to be noted that this means a higher resistance and a sacrifice of the power output. For this assembly, a Bismuth based solder alloy with the composition 57Bi 4Sn 1Ag is used to minimize the electrical contact resistance between interconnect (Cu wire) and thermoelectric element. A thin layer of an insulating adhesive is applied on the Copper bar which serves a two-fold purpose. It acts the holding material of the thermoelectric elements and also prevents shorting of the electrical circuit.
The final assembled prototype can be seen in Figure 5.8b. Packaging of any product is as important as its functional components. For the assembled prototype, packaging has been done as per the schematic shown in Figure 5.8c, where bottom and top plates of Aluminum Nitride (good thermal conductors) are used. Metal spacers are used on which the top Aluminum Nitride (AlN) plate is glued. The metal spacers ensure sufficient air for the heat loss from the thermoelectric elements.

Wireless sensors/Power management systems from two different vendors have been procured and can be seen in Figure 5.9 along with the packaged prototype. Product ‘A’ shown in Figure 5.9a is a temperature and humidity sensor that can be powered by TEG whose output voltage is stepped up using a DC/DC converter. The module has a cyclic wake up, whose duration can be configured by each user, after which the status of temperature sensor is read. A radio telegram is transmitted in case of a significant change of the measured temperature. In case of no significant change, a redundant transmission signal is sent after a particular number of wake-up cycles (also user configurable) to announce the current temperature. Product ‘B’ is a circuit board featuring a DC/DC converter and additional power storage components to manage the surplus energy from
TEG and extend the life of a battery installed on it. It has an indicator BAT_OFF that stays high when harvesting energy and remains low when not harvesting from the TEG.

Figure 5.9 (a) Product A, a wireless temperature sensor along with DC/DC converter (b) Product B, a demo circuit board comprising the power management system

Figure 5.10 (a) Temperature telegram sent by the wireless sensor, (b) BATT_OFF signal turning HIGH when connected with the thermal harvester

Both these products are tested with the assembled prototype as power source and the corresponding data telegram and battery in-use indicator signal are shown in Figure 5.10 a& b respectively. Data points in Figure 5.10a at regular time intervals implies the adequacy of power
supply from the TEG and the BATT_OFF signal in Figure 5.10b turning high when connected with TEG suggest that it is harvesting the thermal energy.

5.6. Scope for Future work - Assembly design for Scaling up

A fabrication process is developed for scaling up the manufacturing of TEG. This is a big challenge due to the poor machinability of Bismuth telluride thermoelectric material manufactured by zone melting method. It is very brittle to handle and is extremely difficult to obtain samples with dimensions in microscale range. Manufacturing Bismuth Telluride by hot extrusion method is known to have better mechanical properties [206, 207]. Rectangular ingots, manufactured by hot-extrusion process, with a cross-section 5 X 5 mm² have been procured from a commercial vendor. Using diamond saw-cutting and sandpaper polishing, rectangular slabs of thickness around ~ 200 µm are obtained from the ingots. Specifically, two new assembly designs are developed that will be essential for automated manufacturing, because these designs are unique in the prior and relevant art. The process routines developed for this device assembly are shown in Figure 5.11

Preliminary activities on the process described in Figure 5.11 are performed. Laser based micromachining and reactive ion etch (RIE) processes are found to be promising techniques for this design. The results are shown in Figure 5.12 below. Figure 5.12 a shows a thick telluride slab before machining. Figures 5.12b & c show examples of laser micromachining of the slabs with controllable pitch between the thermoelectric elements.
Figure 5.11 Process routing showing in-plane sub assembly of a single stack and assembly of multiple stacks for mass manufacturing

Figure 5.12 (a), (b) & (c) Laser micromachining based scaling of the product, (d) & (e) SEM images showing the results of Reactive Ion Etch process using Ar/Cl₂ plasma
Reactive Ion Etch (RIE) process also yielded good exploratory results. A physical mask is attached on selected areas of the thermoelectric slab as shown in Figure 5.12d. These are then etched in Ar/Cl₂ plasma for 20 minutes and the resulting etched profile is shown in Figure 5.12e. A trench of depth ~ 45 µm is obtained that implies an aggressive etch rate with an excellent anisotropic characteristic. Using the RIE process enables us to go to dimensions in the order of hundreds of microns. It is to be mentioned that Seebeck coefficient of Bismuth Telluride manufactured by hot-extrusion is inferior (~150-180 µV/K) when compared to that manufactured by Zone melting method (~200-220 µV/K). But, the ability to go to much smaller widths compensates for the Seebeck coefficient by increase in the thermal resistance and hence the temperature drop ∆T.

5.7. Conclusion

In this chapter, a novel Thermoelectric Energy Conversion (TEC) device is presented. It boasts a design that takes advantage of the size effect on heat transport in solids. The cumulative effect of the increased thermal resistance and increased heat transfer coefficient results in few orders of magnitude higher temperature differential when compared to the current state of art commercial TEC devices. A prototype is built as a proof-of-concept device using micro-machined thermoelectric elements. The results showed superior performance of this device when compared with leading products in the market. Fabrication process for further miniaturization and mass manufacturing is developed to give a scalable process with a high throughput. Application of the prototype is demonstrates in real life applications like data centers, wireless sensor networks (WSN). Successful functioning as power supply to existing commercial wireless sensors proves the compatibility of device.
6. Evidence of Ballistic Transport at Room Temperature

6.1. Introduction

In solids, heat is conducted by electrons and phonons. In metals, electrons are the dominant heat carriers while in semiconductors and dielectrics it is the phonons that carry the majority heat. These phonons interact with other phonons, lattice defects, crystal boundaries and these events are typically referred as scattering processes. These scattering processes are classified as N-(normal) process (phonon momentum is conserved) and Umklapp process (phonon momentum is not conserved). The average distance they travel between each scattering event is called the mean free path. Phonon transport in solids has three possible mechanisms: a) by ballistic transport i.e. the phonons travel through the solid without any interaction, b) by second sound where the energy transport is a wave like phenomenon; this happens when the phonon momentum is conserved during most of the scattering process and c) by diffusion which is observed in almost all the bulk materials. However, the phonon mean free path at room temperature is typically in the order of \(~100\text{nm}\) [208, 209]. Also, scattering is extremely sensitive to microstructural defects. Therefore, ballistic transport and second sound are observed at very low temperatures and in materials of high purity. When the characteristic size of the solid is much larger than the mean free path of the phonon, which is generally the case in most of the heat conductors, there is massive scattering and the heat flow is diffusive. In nano-systems where the solid size is lesser or comparable to the phonon mean free path, heat conduction contains a major ballistic part. Studies have shown ballistic-diffusive phonon transport at room temperature in nanostructures [35-37] and two-dimensional materials like graphene [210, 211].
Fourier’s law of heat conduction, given by Equation 6.1, assumes local thermal equilibrium and reckons the heat flow to be diffusive in nature. In a solid with thermal conductivity $\kappa$, it defines the heat flux vector $\mathbf{q}$ is proportional to the temperature gradient $\nabla T$ in the material. Derived from the kinetic theory, the thermal conductivity is related to other physical properties as in Equation 6.2.

$$\mathbf{q} = -\kappa \nabla T$$ \hspace{1cm} (6.1)

$$\kappa = \frac{1}{3} C v \lambda$$ \hspace{1cm} (6.2)

$C$ is the specific heat per unit volume of the material, $v$ is the speed of sound in the material and $\lambda$ is the phonon mean free path. In the case of ballistic phonon transport, the Fourier law breaks down and is known to over-predict the thermal transport [212, 213]. In such cases, the Boltzmann Transport Equation (BTE), given below by Equation 6.3, has to be solved to study the thermal transport.

$$\frac{\partial f}{\partial t} = \mathbf{v}_g \cdot \nabla f + \frac{\partial \mathbf{k}}{\partial t} \cdot \nabla_k f = \left| \frac{\partial f}{\partial t} \right|_{\text{collision}}$$ \hspace{1cm} (6.3)

$f$ is the phonon distribution function dependent on position vector $\mathbf{r}$, time $t$, wave vector $\mathbf{k}$ of the phonons. $\mathbf{v}_g$ is the group velocity vector of phonons which is defined as

$$\mathbf{v}_g = \frac{\partial \omega}{\partial \mathbf{k}}$$ \hspace{1cm} (6.4)

$\omega$ is the phonon frequency. The right hand side (RHS) of Equation 6.3 denotes the change in the phonon distribution due to the collisions. There are several approaches to solve the BTE using various approximations since a direct analytical solution to its raw form is not practical. Few of them include the relaxation time approximation [214], neglecting the optical phonons, isotopic
approximation [215] and gray approximation where the relaxation time and phonon velocity are taken to be frequency independent. Literature exists on computational studies of thermal transport in ballistic regime [36, 216-218]. It is widely accepted that phonons have majority states with mean free paths in the order of ~100nm. Despite that, a minority of phonon states exist with mean free path as big as 10 µm at room temperature and still have a strong contribution to thermal conductivity of the solid [219]. Such large mean free paths are traditionally believed to exist only at low cryogenic temperatures due to elimination of high frequency phonons with very short mean free paths. There is a paucity of experimental evidence of long mean free paths at room temperature. Recently, Hsiao came up with results showing ballistic thermal conduction at room temperature in SiGe nanowires persisting over 8.3 µm [220]. Nanostructures and cryogenic temperatures have a limited utility to direct applications owing to impractical size and temperatures.

In this chapter, we present the experimental observation of ballistic phonon transport at room temperature in a bulk Lithium Niobate crystal observed at lengths > 500 µm. Lithium Niobate is a dielectric material which is vastly used in optical wave-guides due to its favorable piezoelectric, optical, electro-optic and photorefractive properties. It has non-linear optical properties which makes it an encouraging material for conversion of thermal radiation [221]. It is also cheaply available with a very high Curie temperature (~1500 K) [222] that makes it favorable for applications in high temperature devices.

From a classical point of view, ballistic transport should offer no resistance to heat conduction. But, according to the Landauer formalism quantum confinement restricts the thermal conductance in a channel due to the geometric boundaries. We demonstrate a series of experiments that manifest ballistic thermal transport at room temperature. We use Infrared
Microscopy with Indium-Antimonide (InSb) detector, cooled by liquid nitrogen, which detects radiance from the sample and measures the temperature.

6.2. Experiments

6.2.1. In-plane ballistic transport

Figure 6.1 Schematic of the patterned metal heater and sensors on Lithium Niobate (LiNbO\textsubscript{3}) substrate

Figure 6.1 shows a zig-zag patterned metal heater and a series of metal-strips (resistance type temperature sensors) that act as heat-sinks. When a source current is passed through the heater, its temperature increases due to Joule heating thereby which excites the phonons in that region that propagate until they scatter at a boundary. For the given configuration, the nearest boundary for phonon scattering is the metal Niobate interface at the heat-sink films. Therefore, for ballistic transport, we would not expect any appreciable temperature gradient in the region from the heater to the heat sink, and larger temperature rises in the heat sink where all the transported heat would accumulate upon scattering. Following the same logic, diffusive transport will exhibit a
temperature gradient if the distance between the heater and the heat sink is considerably larger than the typical phonon mean free path of about 100nm. The experiments were performed by passing DC current for a steady temperature in the heater. Figure 6.2a shows IR image of the thin film heater and heat sink on Lithium Niobate substrate. Conventional wisdom would suggest that the zig zag heater lines would heat up the entire area so that the small space between two heater lines will assume temperature very close to the metal lines. However, the thermal image shows large temperature gradient between the heater lines (30 µm distance) and more intriguingly, the region between the heater and the heat sink also showed strikingly small (about 3K) temperature rise. To highlight this anomalous thermal response, we performed a finite element simulation of the experimental conditions, keeping the same geometric and thermal boundary conditions, except considering classical, diffusive transport with the thermal conductivity of 4 W/m-K as given in the literature [223]. Figure 6.2b shows the temperature map of the same geometry from a COMSOL simulation based on diffusive transport. The stark contrast between the two temperature profiles is discernible in Figure 6.2c. The simulation shows a localized heating in the heater region with a gradual temperature gradient and no peaks near the heat-sinks. The IR image shows a little elevation in the temperature of the substrate but a significant jump near the edge of the heat-sink films. This shows that the phonons propagate in a ballistic manner and only scatter at the crystal boundary, the metal heat-sink films in this case.
6.2.2. Cross-plane ballistic transport

The above experiment has the heater and sensor on the surface of Lithium Niobate substrate which demonstrated the in-plane ballistic transport. In the current experiment, we conduct an experiment to investigate if the ballistic mode is dominant in the cross-plane too. A Resistance Temperature Detector (RTD) element can act as a heater when passed a direct current (DC) through it. Figure 6.3a shows a cross-sectional image from IR microscope of RTD placed on Lithium Niobate substrate while Figure 6.3b shows the results from COMSOL simulation for the same. The heater is modeled as a body at a homogenous elevated temperature. The heating of
substrate to an increased temperature and temperature gradient along the vertical direction are evident in the simulation results while they are absent in IR micrograph. Figure 6.3c also shows a spike in temperature, as highlighted by red oval, at the edge of substrate. This is due to energy dissipation when the phonons scatter at the substrate boundary. This again reinforces the ballistic transport at room temperature. To further reinstate this phenomenon, we attach a heat-sink (different materials like carbon tape, kapton foil and glass piece) to the other side of Lithium Niobate substrate. It can be seen in Figure 6.4a,c,e and the corresponding temperature profiles in Figure 6.4b,d,f that the heat sink is heated to a higher temperature than the actual channel of heat flow i.e. LiNbO$_3$ substrate itself. LiNbO$_3$ is still at room temperature (~30° C) while the carbon tape that is in contact with the substrate on the opposite side is at ~40° C and the same observation is found in the case of Kapton foil and glass piece too.

Figure 6.3 (a) IR thermal image of RTD heating on Lithium Niobate substrate, (b) temperature distribution from the COMSOL simulation, (c) temperature profile along the line scan in (a)
6.2.3. Thermal Conductivity variation with length

Thermal conductivity of the solid is known to vary with its characteristic length in the ballistic regime [35, 220]. Computational studies of this size effect on thermal conductivity exist in the literature [224, 225]. $3\omega$ method [35], coherent heating using X-ray beams [37] are some of the techniques used experimentally. Though most of these study the ballistic transport in length scales $\sim$100-200 nm, the largest mean free path below which ballistic transport is observed is 8.3 µm in the case of SiGe nanowires [220]. In the current experiment, a Lithium Niobate specimen is cut in a rectangular shaped cross-section with an aspect-ratio long enough to approximate the phonon transport to be one-dimensional. For the case of diffusive mode of transport, the temperature profile in the specimen can be modeled as a conduction problem in extended surfaces. This methodology to evaluate the thermal conductivity of a material has yielded good results in our previous works [43, 226].

The experimental set-up shown in Figure 6.5a has a sample, which is few millimeters long with cross-section 250 µm X 250 µm that is mounted on a piezo-controlled stage with a fixed end and a variable end. The sample is attached to the fixed end using a carbon based adhesive while is left free on the other side. The free-standing part of the sample between the two ends is considered the length, $L$, which is varied in this experiment. A RTD element, the same as discussed in the previous section, is used as heater. The heater is brought in contact from the top side of sample supported at the variable end. A direct current (DC) of 25 mA amplitude is sourced to the RTD element and is held consistent at each length. This ensures the heater is at the same temperature in all the cases to eliminate any change in thermal conductivity with temperature. This is repeated at five different lengths of the sample viz. $L_0$, $L_1$, $L_2$, $L_3$ and $L_4$, listed in the ascending order.
Figure 6.4 (a), (c) & (e) IR thermal images of RTD heating on Lithium Niobate (LiNbO3) with a heat sink on the other side (b), (d) and (f) corresponding temperature profile along the line scans.

The temperature profile in a one-dimensional rectangular fin can be modeled as

\[
\frac{T(x) - T_\infty}{T_b - T_\infty} = \frac{T_L - T_\infty \sinh(mx) + \sinh(m(L-x))}{\sinh(mL)}
\]  

(6.5)

where \( T(x) \) is the temperature at \( x \) along the length of the sample specimen, \( T_b \) is the base temperature, \( T_L \) is the temperature at the heated location, and \( m \) is a constant related to the fin geometry.
temperature at $x=0$, $T_L$ is the tip temperature at $x=L$, $T_\infty$ is the ambient temperature and $m$ is expressed as

$$m = \sqrt{\frac{hP}{\kappa A_c}}$$

(6.6)

$h$ is the overall heat transfer coefficient, $P$ is the perimeter and $A_c$ the cross-sectional area of the sample. $h$ and $\kappa$ are the only two unknowns in Equations 6.5 and 6.6.

Figure 6.5 (a) Set-up of the sample on piezo-controlled stage, (b) & (c) IR micrographs of the heated sample at length $L=L_0$ and $L=L_4$ respectively, (d) & (e) fit of the model prediction to the experimental temperature profiles at lengths $L_0$ and $L_4$, (f) thermal conductivity variation with length of the free-standing sample specimen
Evaluation of $h$ is discussed in detail by in earlier chapters. In our previous work [129], it was shown that in a micro specimen the value of heat transfer coefficient is primarily governed by the size of heat source and is $\sim 110 \text{ W/m}^2\text{K}$ for RTD element. We proceed with the same value and adopt parametric variation of $\kappa$ to get the best fit of model prediction to the experimental temperature readings. Figures 6.5b and 6.5c show the IR images of the sample heated at lengths $L_0$ and $L_4$ respectively. The standard of the fit between the model prediction and the experimental data is shown in Figures 6.5d and 6.5e for the corresponding values of thermal conductivity. Figure 6.5f depicts the variation in thermal conductivity with the length of the free-standing part of the specimen.

The literature is rare for measurement of thermal conductivity in Lithium Niobate. Wong [223] reports the thermal conductivity values previously measured by two techniques at different temperatures. Values of $(10-11) \times 10^{-3} \text{ cal/s-cm-}^\circ\text{C}$ are reported at temperatures around $30^\circ\text{C}$ which translates to $\sim 4-4.5 \text{ W/m-}^\text{K}$. The commercially available Lithium Niobate has its thermal conductivity in the same range as well.

It has been well documented and also discussed earlier that the Fourier law tends to overestimate the heat flux and hence breaks down in the ballistic transport regime. There have been attempts to employ the Fourier’s law with a correction term to thermal resistance of the sample [37, 227]. Figures 6.5d and 6.5e show the experimental temperature profile along with the prediction of model, given by Equation 6.5, for thermal conductivity values of bulk sample ($\kappa_{\text{bulk}} = 4 \text{ W/m-}^\text{K}$) and the best fit curve ($\kappa_{\text{app}}$) at the corresponding sample length. We define the thermal conductivity value that fits best to the experimental temperature distribution as ‘apparent thermal conductivity $\kappa_{\text{app}}$’. It is observed that using $\kappa_{\text{bulk}}$ in Equation 6.5 overestimates the temperature distribution and the difference between $\kappa_{\text{bulk}}$ and $\kappa_{\text{app}}$ is decreased with an increase in length. This
variation in thermal conductivity is plotted in Figure 6.5f. Thus, it is shown that the Fourier law can still be employed in ballistic-diffusive regime but with a corrected value of thermal conductivity. Lack of consensus between the calculated thermal conductivity and bulk thermal conductivity indicates the presence of active ballistic transport mode even at large length scales.

### 6.2.4. Heat Pulse Experiment

All the experiments discussed up to this point are based on IR microscopy and one cannot be conclusive by relying on a single experimental technique. We provide qualitative results from a heat pulse experiment that corroborate the dominance of ballistic phonon transport at room temperature. Heat pulse experiments date back to a few decades that are traditionally used in detection of second sound [228, 229] in solids. However, these experiments use high purity crystals cooled to ultra-low temperatures. The sample preparation for this experiment begins with depositing metal heater and sensor films on the solid substrate of interest. A typical heat pulse experiment involves supplying a pulsed heat current in the heater furnished by electrical current of similar waveform. The resistance signal in the sensor serves as an indicator for temperature evolution with time. Figure 6.6a shows the experimental set-up and Figure 6.6b show the results reported by Jackson [230] in very pure NaF at cryogenic temperatures.

Here, a heat pulse of 2 millisecond duration (8 milli-amp current pulse) is passed through the metallic film heater. This is shown in Figure 6.6d. As soon as the thermal pulse is activated in the heater, it will then travel through the material. If the material shows ballistic heat transfer (Figure 6.6c), then this pulse will not broaden or diffuse. It will show two peaks, small one coming from longitudinal phonons and the bigger one from transverse phonons. The sharpness of the peaks represent how ballistic is the heat transfer. Figure 6.6c also shows how the heat pulse
would be sensed if the heat transfer were diffusive. Our experimental results are shown in Figure 6.6e, which clearly shows highly ballistic or heat super conduction at room temperature. Appearance of a single peak in the sensor response indicates the presence of only a single phonon mode, either transverse or longitudinal.

Figure 6.6 (a) Set-up of heat pulse experiment, (b) Results of heat pulse experiment in very pure NaF reported by Jackson et al [230], (c) Expected response curve for ballistic and diffusive mode, (d) Response of the heater during the current pulse, (e) Response of the sensor for the corresponding heat pulse
6.3. Discussion

Various studies have emerged, both on the computational and experimental fronts, to explore the phonon heat transport in ballistic regime [46, 231-233]. Not all phonons contribute equally to the heat transport. Though there is a quantitative mismatch between the studies with mean free path values lying in the domain of few nanometers to lengths as long as 10 µm, most of them concur to the fact that low frequency phonons contribute substantially to heat transport. Packets of phonons with long wavelengths can travel for long distances without breaking apart.

Lithium Niobate is generally synthesized in two compositions viz. the congruent and the stoichiometric. The phonon characteristics of LiNbO$_3$ and the influence of composition has been well established using techniques like Raman spectroscopy [234], IR spectroscopy [235]. The phonon density of states (DOS) has also been calculated using ab initio method [236]. The total density of states display the predominance in the low-frequency region. Niobium and Lithium atoms vibrate at low frequencies attributed to the large atomic mass and small force constants respectively. It is the oxygen atoms that majorly occupy the high-frequency region. Scattering phenomenon is known to have a big role in filtering or suppressing the contribution from high-frequency phonons. Alloy scattering [220], defect scattering [237] are known to enhance this suppression. Lithium Niobate is recognized to have a high density of sub-microscopic defects that are intrinsic [238-240] some of which may or may not depend on the crystal composition. We hypothesize this high defect concentration is responsible for the restraining of high-frequency phonons. LiNbO$_3$ is an anisotropic material and is found to exhibit strong phonon focusing [241]. In the Raman spectrum, only transverse phonons are detected in one geometry while both transverse and longitudinal phonons are detected in other geometries [234]. This
argument is further strengthened by the display of only one sharp peak shown in Figure 6.6e, in the heat pulse experiment.

To the best of our knowledge, this is the first experimental evidence of ballistic heat transfer in bulk crystals at room temperature. Even though the research has been for many decades, ballistic heat transfer has been limited to around 4 K temperature. The impact of a heat superconductor is immense on thermal management (electronics and power electronics) and phononics (heat counterpart of electronics) such as thermal transistor, thermal logic gate and memory, impossible at room temperature. If 1 µm electron mean free path in graphene gives the highest-mobility (>200,000 cm² V⁻¹ s⁻¹), the >500 µm mean free path of phonons in this research will revolutionize phononics even without any need for nanoscale size or ultra-cold temperatures.
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