ZnO-based Thermoelectrics: Modelling, Electrochemical Thick Film Growth, and Characterization

by

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Abstract

The thermoelectric performance of electrodeposited, aluminum doped zinc oxide was assessed. In this work, wurtzite ZnO was first modelled using Mueller-Plathe to compare the effectiveness of different nanostructured configurations on reducing thermal conductivity. A new analysis technique, Local Vibrational Density of States Equilibrium Molecular Dynamics (LVDOS-EMD), was created to study localized lattice vibrations around nanostructural features of silicon and ZnO, and was used to predict thermal properties in materials of similar composition $17 \times$ faster than conventional thermal modelling methods. A 30% void density was determined to yield the best reduction in thermal conductivity by volume of voids in bulk Al:ZnO with a computed thermal conductivity of 0.77 W m$^{-1}$ K$^{-1}$ at room temperature, 3$\times$ below the threshold achieved through established experimental means with high electrical conductivity Al:ZnO.

Thick film, electrodeposited Al:ZnO was grown using a nitrate system. Experiments on solution pH using various counter electrodes demonstrated that inert electrodes caused acidification of the growth solution, limiting film thickness. Chloride contamination from commonly used Ag/AgCl reference electrodes was also determined to affect thick film opacity, morphology, crystallinity, and electrical properties. Aluminum integration and activation was explored by adding Al(NO$_3$)$_3$ to the growth solution during film synthesis, yielding aluminum integration molar ratios of up to 1.72% (Al$_{0.034}$Zn$_{0.966}$O). Partially doped films in excess of 95µm thick, 4$\times$ the thickness reported elsewhere, were electrochemically grown and characterized. Sub-micron voids were integrated into the films using sacrificial material and annealing. A new electrochemical chromium etching methodology was developed and successfully used to free 20 films from their growth substrates for thermoelectric characterization.

A new, reusable thermoelectric test apparatus for thin film thermoelectric testing was designed, implemented, calibrated, and successfully deployed to characterize ZnO and Al:ZnO thin films grown 79 - 95µm in thickness. Extremely low thermal conductivity of 11 mW m$^{-1}$ K$^{-1}$ at room temperature was demonstrated concurrently with a Seebeck coefficient of
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−88 μV K⁻¹. Polycrystallinity and poor dopant activation yielded a low electrical conductivity of 0.75 mS/cm and corresponding low room temperature ZT of $1.3 \times 10^{-5}$ for the Al:ZnO films.
Preface

Statement of Contributions

Some energy dispersive x-ray spectroscopy results discussed in Section 3.4 were performed by Dr. Suresha Mahadeva. Ms. Valerie Siller performed some experimental work under my supervision, including Al:ZnO film growth, microscope photographs, electrical resistance measurements of films and interface materials, and chromium etching experiments presented in Sections 3.4, 3.5, and 4.1.

List of Publications or Submissions

Some of the work presented throughout this dissertation has text and/or figures derived from the following papers:

- Section 3.4: Christoph Sielmann, Valerie Siller, Boris Stoeber, and Konrad Walus. Thick Film Electrochemical Growth of Al-Doped Zinc Oxide. Submitted, 2016
List of Publications or Submissions

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$\alpha$  Seebeck Coefficient [V/K]

$\beta$  Proportional velocity analogous to group velocity

$\kappa$  Thermal conductivity tensor

$\nabla T$  Temperature gradient

$D(q)$  Dynamical matrix

$e(q,m)$  Eigenvectors of the Dynamical Matrix

$Q$  Heat flux vector

$q$  Phonon wavevector

$r_0(j)$  Initial position of a unit cell

$u(j,i;t)$  Displacement of an atom from its mean average position

$\eta$  Efficiency

$\gamma$  Adjustment factor for efficiency calculation

$\kappa$  Thermal conductivity [W/mK]

$\omega$  Angular frequency

$\rho$  Electrical resistivity [$\Omega$cm]

$\sigma$  Electrical conductivity [S/cm]

$\sigma$  Stefan-Boltzmann constant

$\tau(q,m)$  Phonon lifetime

$\xi$  Structural Thermoelectric Enhancement Factor (STEF)

$\zeta$  Proportional rate of scattering into a segment
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<tr>
<td>$A$</td>
<td>Cross-sectional area [$m^2$]</td>
</tr>
<tr>
<td>$a$</td>
<td>Atom iterator or overlap-corrected width of a segment</td>
</tr>
<tr>
<td>$A_{\text{closed}}$</td>
<td>Total contact surface area between the heater element and the base plate</td>
</tr>
<tr>
<td>$A_{DUT}$</td>
<td>Device under test cross-sectional area</td>
</tr>
<tr>
<td>$b$</td>
<td>General purpose iterator</td>
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<tr>
<td>$C(q,m)$</td>
<td>Modal heat capacity of the material</td>
</tr>
<tr>
<td>$D$</td>
<td>Density of states</td>
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<tr>
<td>$D$</td>
<td>Notch depth</td>
</tr>
<tr>
<td>$d$</td>
<td>Distance</td>
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<tr>
<td>$E$</td>
<td>Energy</td>
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<tr>
<td>$e$</td>
<td>Emissivity</td>
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<tr>
<td>$f$</td>
<td>Regression linear fit</td>
</tr>
<tr>
<td>$I$</td>
<td>Electric current $A$</td>
</tr>
<tr>
<td>$i$</td>
<td>General purpose iterator</td>
</tr>
<tr>
<td>$j$</td>
<td>General purpose iterator</td>
</tr>
<tr>
<td>$K$</td>
<td>Thermal conductance [$W/K$]</td>
</tr>
<tr>
<td>$k$</td>
<td>General purpose iterator or nanowire diameter</td>
</tr>
<tr>
<td>$L$</td>
<td>Length [$m$]</td>
</tr>
<tr>
<td>$l$</td>
<td>Mean free path</td>
</tr>
<tr>
<td>$M$</td>
<td>Mass</td>
</tr>
<tr>
<td>$m$</td>
<td>Phonon mode</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of particles or objects within the specified system</td>
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<tr>
<td>$p$</td>
<td>Notch period</td>
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<td>$P_s(\omega)$</td>
<td>Probability of a wavelet surviving segment $s$</td>
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<tr>
<td>Q</td>
<td>Thermal power [W]</td>
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<td>$Q_H$</td>
<td>Thermal power from a heater [W]</td>
</tr>
<tr>
<td>$Q_s(\omega)$</td>
<td>Probability of a wavelet surviving exactly $s$ segments</td>
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<tr>
<td>$R$</td>
<td>Electrical resistance [Ω]</td>
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<tr>
<td>$R_{HI\text{ratio}}$</td>
<td>Ratio between heater element thermal resistance and interface thermal resistance</td>
</tr>
<tr>
<td>$S$</td>
<td>Total number of segments along a material</td>
</tr>
<tr>
<td>$s$</td>
<td>Segment of a larger whole, or general purpose iterator</td>
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<tr>
<td>$T$</td>
<td>Temperature [K]</td>
</tr>
<tr>
<td>$T(q,m;t)$</td>
<td>Kinetic energy for the given mode and time</td>
</tr>
<tr>
<td>$U(q,m;t)$</td>
<td>Potential energy for the given mode and time</td>
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<tr>
<td>$V$</td>
<td>Volume</td>
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<tr>
<td>$v_g(q,m)$</td>
<td>Modal phonon group velocity</td>
</tr>
<tr>
<td>$V_{ac}$</td>
<td>Alternating current voltage [V]</td>
</tr>
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<td>$V_{dc}$</td>
<td>Direct current voltage [V]</td>
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<tr>
<td>$W$</td>
<td>Available work/power [W]</td>
</tr>
<tr>
<td>$w$</td>
<td>Notch width or time window size</td>
</tr>
<tr>
<td>$Z$</td>
<td>Thermoelectric figure of merit [1/T]</td>
</tr>
<tr>
<td>$Z_a$</td>
<td>Velocity autocorrelation function to atom $a$</td>
</tr>
<tr>
<td>$Z_s$</td>
<td>Probability of a particle surviving segment $s$ without collision</td>
</tr>
<tr>
<td>$ZT$</td>
<td>Unitless thermoelectric figure of merit</td>
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I wish to thank my supervisors, Dr. Konrad Walus and Dr. Boris Stoeber, for taking a chance on a hypothesis with great potential and moderate risk. Their insights, patience, support, and understanding have been instrumental in every success throughout the project. I wish to thank Valerie Siller for her experimental contributions, rigorous scientific standards, and general enthusiasm for the work. Her willingness to travel overseas and dedicate herself fully to a challenging project in a foreign language demonstrates outstanding character. I wish to thank Dr. Suresha Mahadeva and Dr. Lisheng Wang, who both provided insights into the material science involved in the project and assisted with some of the characterization measurements. I would like to acknowledge funding, equipment, and facilities provided by Natural Sciences and Engineering Research Council (NSERC), the Canadian Foundation for Innovation (CFI) and the University of British Columbia through the Four Year Fellowship Program. Simulation time was provided by Computing Canada Westgrid clusters. I wish to thank my lab colleagues, particularly Anas Bsoul, Simon Beyer, and Andrew Cavers, all of whom provided advice or a sympathetic ear depending on the complexity or persistence of the problem. Finally, I wish to thank my family for their support and unwavering patience, and my wife, Sara, without whom this work would not have been possible.
Dedication

In dedication to my exceptionally patient and endlessly supportive wife, Sara.
Chapter 1

Introduction

1.1 Motivation

An ongoing challenge today is the pursuit of greater quantities of clean, usable energy. Transportation, manufacturing, heating and cooling, medical services, and primary resource extraction are critical, energy-intensive endeavours that continue to demand significant power. Many of the current methods employed to extract usable energy from resources such as fossil fuels yield waste heat during the process. As an example, average fossil-fuel driven power plants only extract 40% of the available chemical energy from their fuel, relegating the remainder as waste heat expelled through steam or as heated water into heat sinks such as lakes[3]. If all industries are considered then approximately 70% of the world’s energy is wasted as heat[4]. Limitations in existing technology limit efficiency, portability, longevity, and safety in large-scale energy production facilities that depend on heat to produce usable power. New, solid state technology that can scale cost effectively with power demand could see applications ranging from portable waste heat recovery to large scale power generation[5]. A comparison between common heat to power conversion technologies can be found in Figure 1.1.

Thermoelectric materials convert a thermal gradient into an electric potential through the Seebeck effect. It is an old technology which is used in applications including small-scale nuclear thermoelectric generators, such as those found on the Voyager I and II spacecraft, solid state cooling through a related Peltier effect, and temperature sensing through the ubiquitous thermocouple. Research in the 1990s spurred a renaissance in the field of thermoelectrics as researchers determined that small-dimensional structures such as quantum dots and nanowires have the potential to yield far more efficient thermoelectric materials[7].

Active thermoelectric companies, such as Alphabet Energy, GMZ Energy, and Laird Technologies are developing thermoelectric devices based on nanostructured materials for thermoelectric power generation[8][9], automotive energy recovery[10][11], military waste heat recovery[12], diesel generators, industrial machines, and the oil and gas sector[13]. Alphabet Energy
1.1. Motivation

Figure 1.1: Plot showing the conversion efficiency of a variety of heat to electricity conversion systems[6]. The dimensionless thermoelectric figure of merit, $ZT$, is also shown, representing the $ZT$ required for a thermoelectric module to achieve comparable efficiency.

recently commercialized a 25 kW electrical output per 1000 kW waste heat thermoelectric generator (TEG) targeting oil and gas applications and is focusing their research and development on low cost thermoelectric materials that do not require exotic elements[8]. Laird Technologies has commercialized a series of low power thin film thermoelectric modules for commercial applications. Although they still operate at low efficiencies compared to mechanical methods of power generation, their small scale and flexible design opens up new markets for waste heat recovery[5].

The performance of a thermoelectric module is determined by its dimensionless figure of merit, $ZT$, where module efficiency approaches Carnot efficiency as $ZT$ approaches infinity. A recent study on the economics of thermoelectrics suggest that modules demonstrating $ZT > 1$ are already cost competitive in some sectors for power generation, provided that the modules can be scaled up appropriately[14]. With the increase in thermoelectrics research, there have been numerous publications within the last 10 years highlighting materials with $ZT > 2$, although these experiments
1.2 Background

are often difficult to reproduce, which complicates integrating these new materials into commercializable modules[15]. One of the best performing thermoelectric modules has a reported $ZT = 1.96$ and is based on superlattice nanomaterials[14].

With increasing industrial and academic interest, international funding has increased as well. The global thermoelectric market was worth $364.1$ million USD in 2014 and is expected to reach $763.5$ million USD by 2022[5]. Zervos and Harrop have proposed that integration of thermoelectric modules in vehicles for waste heat recovery may happen as soon as 2020, and with the continued growing interest in clean energy technologies, it is likely that interest in low cost, environmentally friendly, high efficiency thermoelectric materials will continue to expand. Further advances in thermoelectrics could lead to solid state replacements for many mechanical systems associated with power generation, such as steam turbines, as solid state alternatives that require less maintenance and operate more safely. Smaller scale systems for heat recovery and personal power generation could also be realized, affording greater independence from central power generation and reducing wasted energy from transmitting power long distances. Developing these opportunities through the design and fabrication of efficient, cost-effective thermoelectric materials primarily motivate this work.

1.2 Background

1.2.1 Thermoelectric Theory

Thermoelectricity involves the conversion of a thermal flux into electricity. Typical thermoelectric power generation and cooling modules comprise of numerous thermocouples connected thermally in parallel and electrically in series or parallel depending on the desired operating voltage of the module. Thermocouples consist of a hot junction and a cold junction, with dissimilar materials, typically n-doped and p-doped semiconductors, as shown in Figure 1.2. Electronic majority charge carriers, electrons and holes for n-type and p-type materials, respectively, diffuse with the thermal gradient to produce a net current through the device. Concurrently, heat propagates from the hot junction ($x = L_{p,n}$) to the cold junction ($x = 0$), reducing the overall efficiency of the module. As the electrons travel through each leg of the thermocouple, electrical resistance in the material dissipates electron energy, also reducing the overall efficiency of the module.

The heat power into the module from the surface of the thermoelectric module, $Q_p$ and $Q_n$, for the p-type and n-type legs respectively, consumed
Figure 1.2: Simplified thermoelectric power generation module showing electrical connections on either side. Commercial modules typically consist of many such pairs.

by the module are\cite{16}

\[ Q_p = \alpha_p I T_H + \kappa_p A_p \frac{dT}{dL}, \]  
\[ (1.1) \]

\[ Q_n = \alpha_n I T_H + \kappa_n A_n \frac{dT}{dL}, \]  
\[ (1.2) \]

where \( \alpha_x \) is the Seebeck coefficient, \( I \) is the electrical current, \( T_H \) is the temperature at the hot end of the device, \( \kappa_x \) is thermal conductivity, \( A_x \) is the cross-sectional area, \( L \) is the length of the leg, and \( x \) represents the leg material (typically n or p type). The Seebeck coefficient of the material is the open circuit (zero current density) induced voltage per degree of temperature difference between the points of measurement. The coefficient is conventionally determined with respect to another material used in the measurement, and is thus generally known as the relative Seebeck coefficient. The relative Seebeck coefficient is typically expressed relative to platinum, and values reported in this work are thus adjusted. It is possible
1.2. Background

to determine the absolute Seebeck coefficient of a material by measuring its coefficient using a superconducting measurement lead near absolute zero in temperature, but performing this measurement was considered out of scope for this work.

The heat consumption of the device is a sum of \([1.1]\) and \([1.2]\) integrated over the length of the thermocouple, yielding

\[
Q_H = K \Delta T + (\alpha_p - \alpha_n) I T_H - \frac{1}{2} I^2 R, \tag{1.3}
\]

where \(R\) is the electrical resistance of the module, \(K\) is the thermal conductance, and \(\Delta T\) is the difference in temperature along the length of the device. The electrical power produced under ideal conditions is

\[
W = I \left[ (\alpha_p - \alpha_n) \Delta T - IR \right], \tag{1.4}
\]

where \(W\) is the electrical power available from the module. The module efficiency is

\[
\eta = \frac{W}{Q_H} = \frac{I \left[ (\alpha_p - \alpha_n) \Delta T - IR \right]}{K \Delta T + (\alpha_p - \alpha_n) I T_H - \frac{1}{2} I^2 R}. \tag{1.5}
\]

If the module is operated at peak efficiency by selecting a matching load

\[
R_{load} = \gamma R, \tag{1.6}
\]

where

\[
\gamma = \left( 1 + Z \frac{(T_H + T_C)}{2} \right)^{\frac{1}{2}}, \tag{1.7}
\]

then the maximum electrical current, \(I\), electrical power, \(W\), and efficiency, \(\eta\), are

\[
I = \frac{(\alpha_p - \alpha_n) \Delta T}{R(\gamma + 1)}, \tag{1.8}
\]

\[
W = \frac{\gamma \left[ (\alpha_p - \alpha_n) \Delta T \right]^2}{R(\gamma + 1)^2}, \tag{1.9}
\]

\[
\eta_{max} = \frac{(\gamma - 1) \Delta T}{[(\gamma + 1) T_H - \Delta T]} . \tag{1.10}
\]

The figure of merit in units of \(1/\text{K}\), \(Z\), can be determined independently for each leg material using

\[
Z_{p,n} = \frac{\alpha_{p,n}^2}{\rho_{p,n} \kappa_{p,n}}, \tag{1.11}
\]
1.2. Background

and for the entire module using

\[ Z = \frac{(\alpha_p - \alpha_n)^2}{(\sqrt{\rho_n \kappa_n} + \sqrt{\rho_p \kappa_p})^2}, \]  \hspace{1cm} (1.12)\]

where \( \rho_x \) is the electrical resistivity for leg material \( x \). The more conventional dimensionless figure of merit, \( ZT \), can be determined by multiplying \( Z \), which varies with temperature, by the average temperature of the device, \( T \). The module figure of merit is maximized when the product of \( RK \) is minimized, which occurs when leg dimensions are defined using\[ L_n A_p = \left( \frac{\rho_p \sigma_n}{\rho_n \sigma_p} \right)^0.5 . \] \hspace{1cm} (1.13)\]

If the module is optimized for maximum power output rather than maximum efficiency then the load resistance,

\[ R_{\text{load}} = R, \] \hspace{1cm} (1.14)\]

and the resulting current, power, and efficiency are

\[ I = \frac{(\alpha_p - \alpha_n) \Delta T}{2R}, \] \hspace{1cm} (1.15)\]

\[ W = \frac{[(\alpha_p - \alpha_n) \Delta T]^2}{4R}, \] \hspace{1cm} (1.16)\]

and

\[ \eta_{\text{max}} = \frac{Z \Delta T}{4 + ZT_H + Z(T_H + T_C)/2}. \] \hspace{1cm} (1.17)\]

Ideal Carnot efficiency can be represented by

\[ \eta = 1 - \frac{T_C}{T_H}, \] \hspace{1cm} (1.18)\]

and the efficiency of a thermoelectric module as a function of its \( ZT \), representing the dimensionless figure of merit using the average temperature of the device, is

\[ \eta = \left( 1 - \frac{T_C}{T_H} \right) \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_c}{T_H}}. \] \hspace{1cm} (1.19)\]

From (1.19), module efficiency approaches (1.18) as \( ZT \) approaches infinity. A high \( ZT \) can only be achieved by maximizing the Seebeck coefficient and electrical conductivity while minimizing thermal conductivity as shown by (1.11) and (1.12).
1.2. Background

1.2.1.1 Ideal Materials

The characteristics of an ideal thermoelectric material have been well defined\cite{17}, with entropic reversibility being a critical factor for high $ZT$ materials. Highly entropically reversible thermoelectric materials are structured to keep electrons within a very narrow energy range, thereby minimizing entropic losses (heat) when the electrons arrive at the cold junction. The Seebeck coefficient of the material must be non-zero and as large as possible. Similarly, the electrical conductivity of the material must be very large such that no induced electrical power is lost to heat before it leaves the module. Of exceptional importance is the manner in which heat travels through the module. Heat can propagate from the hot junction to the cold junction through phononic or electronic energy transfer. The former is a result of lattice vibrations within the material whereas the latter results from excess energy stored within electrons as they reach the cold junction\cite{16}.

While the electronic contributions to thermal conductivity are often ignored as the phonon contributions are much greater, as thermoelectric materials continue to improve by reducing phonon transport, the electronic contribution becomes more important. Minimizing the electronic contribution to thermal conductivity requires reducing the energy variability of the electrons as they reach the cold junction while concurrently selecting the temperature gradient and vacuum energy, or work function, of the cold electrode to prevent the formation and transmission of hot electrons\cite{17}. These conditions are necessary for the thermoelectric process to be reversible, which is required to minimize non-Carnot entropic losses resulting from the conversion of thermal energy to electrical energy. For example, if the phonon contribution to thermal conductivity is less than $0.5\, \text{W m}^{-1}\, \text{K}^{-1}$ then an order of magnitude reduction in electron energy variation from 250 meV to 25 meV can increase $ZT$ from 3 to 6\cite{17}. Lower phonon contribution to thermal energy increases the significance of this effect, meaning that high efficiency thermoelectric materials exceeding $ZT = 3$ must seriously consider mitigating electronic contributions to thermal conductivity in the material. Some experimental evidence exists to support this model proposed by Humphrey and Linke, reinforcing these conclusions\cite{17–19}.

Reducing electron energy spread is possible using nanostructured materials with reduced dimensionality such as quantum dots (0D), nanowires (1D), and quantum wells (2D)\cite{7}. These materials increase the spread between energy bands available to electrons. Some materials, such as superlattice nanostructures use bandgap tailoring to mask off electrons with lower energy levels by imposing periodic electronic band energy barriers\cite{20}. Prac-
tical materials must also emphasize a reduction of thermal conductivity by interfering with phonon transport and minimizing the spread of electron energy while still demonstrating a large Seebeck coefficient and electrical conductivity.

1.2.1.2 Low Dimensional Materials

A large variety of structures and structural modifications have been explored experimentally and theoretically in an effort to improve performance. Zero dimensional devices such as quantum dots have a delta function electronic density of states, and have been shown in highly controlled environments to have amenable thermoelectric properties\cite{21,23}. One dimensional (1D) structures such as nanowires are easier to fabricate, present a density of states with narrow peaks, and have received the bulk of experimental and theoretical exploration. A subset of nanowires, superlattice nanowires, benefit in that they can provide both zero dimensional (0D) and 1D confinement (depending on size) while also further reducing lattice thermal conductivity through enhanced phonon boundary scattering\cite{18,21,25}. Surface modifications to nanowires have also been a subject of great interest since the experimental work of Hochbaum et al. revealed a 100× reduction in room temperature silicon lattice thermal conductivity\cite{26}. This reduction was achieved by using a wet etch technique to roughen the surface of the nanowires with 2 - 4 nm diameter cavities of unknown depth\cite{26,27}. 2D devices such as quantum wells have been considered, although their performance has yet to compete with devices with greater quantum confinement\cite{19,28,29}. An interesting hybrid material classification is nanobulk materials. These materials are fabricated by fusing nanoscale pellets into bulk structures through a process such as sintering\cite{30,31}. Recent publications using this method have shown very promising results using Al-doped zinc oxide (Al:ZnO)\cite{32}.

Companies such as Alphabet Energy, GMZ Energy, and Laird Technologies are pursuing nanostructured thermoelectric materials, with nanobulk and thin film technologies demonstrating the greatest commercial viability in this category at present\cite{9,12,14}. For large-scale power generation applications, one dimensional structures such as nanowires do not have the cross sectional area necessary to achieve the desired power density for a generator, resulting in a reduction in cost competitiveness for the material\cite{14}. One dimensional structures are also very difficult to integrate into modules and without a filler material must contend with radiative heat transfer through the device. Many publications favourably model the thermoelectric performance of nanowires and superlattice structures, but very little experimental
1.2. **Background**

evidence exists to support these models on the scales necessary to achieve realizable, repeatable quantum effects.

Nanobulk and thin film technologies incorporate nanostructural features within the materials primarily to impede phonon transport without significantly reducing electronic transport by creating scattering sites with impurities or nanovoids embedded into the material[30, 32]. Other methods are also currently under examination to improve thermoelectric performance by introducing nanostructural features to bulk materials, such as inducing mechanical deformations in silicon through the application of high pressure[33], producing nanoscale precipitates in bulk materials[34], forming multi-phase or unstable materials[35], introducing new crystal structures into the material lattice[36], enhancing disorder in the material for phonon band tailoring[37, 38], or increasing the effect of defects on phonon propagation[39]. Some methods, such as the addition of dislocation arrays in bulk bismuth antimony telluride have produced materials with $ZT = 1.86$[38].

### 1.2.2 Zinc Oxide

Zinc oxide (ZnO) is a common, semiconducting, crystalline material with many desirable properties including a large bandgap, optical transparency, high melting temperature, and piezoelectricity. ZnO is a naturally n-doped semiconductor with established and upcoming applications in photovoltaics, microelectromechanical systems, piezoelectric devices, and thermoelectrics[40–44]. Additional doping of ZnO can have significant effects on the structural morphology, optical transparency, and thermal and electrical conductivity of the material[45]. For example, chloride doping of nitrate-based, electrochemically grown ZnO can cap the formation of ZnO nanowires, allowing for the formation of complex tree-like structures[46].

ZnO has a typical electronic bandgap of 3.3 eV and adopts either a zinc blende or wurtzite structure. A wurtzite ZnO unit cell and an orthographic image of a ZnO nanowire are shown in Figure 1.3. The distance between zinc atoms along ⟨100⟩ (a) is 3.25 Å and the distance between zinc atoms along ⟨001⟩ (c) is 5.20 Å[47]. The ratio, $u$, is ideally 3/8 for an ideal wurtzite structure. ZnO can form atomically thin layers while retaining stability and can also be formed into hexagonal nanowires, plates, and pillared structures[40]. Zinc oxide is environmentally friendly, extremely low cost, and is considered to be one of the economically fastest growing oxide materials in industry[12, 48].

Metal oxide thermoelectrics form a material system based on one or
1.2. Background

![Diagram of a wurtzite ZnO unit cell and a slice of a wurtzite ZnO nanowire](image)

Figure 1.3: a) Illustration of a wurtzite ZnO unit cell, b) A slice of a wurtzite ZnO nanowire used for modelling in Chapter[2] with the c-axis aligned vertically, rendered using VMD[49]. Red spheres represent zinc atoms and grey atoms represent oxygen atoms.

Multiple cations bonded with oxygen. Example oxide materials with good thermoelectric properties include zinc oxide (ZnO) (n-type), Na$_x$CoO$_2$ (p-type), Ca$_3$Co$_4$O$_9$ (p-type), SrTiO$_3$ (n-type), and CaMnO$_3$ (n-type)[50]. Oxides have gained substantial interest as thermoelectric materials due to their high temperature chemical stability, low thermal conductivity, chemical resistance, ease of synthesis, high mechanical strength, and moderate to high bandgap[51]. Though not a viable thermoelectric material on its own due to a low electrical conductivity, when doped with aluminum (Al), gallium (Ga), or a mixture of both, bulk zinc oxide can exceed a $ZT$ of 0.3 at $1000^\circ$C[52, 53]. Aluminum-doped zinc oxide (Al:ZnO) shows particularly high promise and is considered to be one of the best performing oxide ther-
1.2. Background

moelectric materials\cite{44, 52, 55}.

1.2.3 Al:ZnO Thermoelectrics

Al doping of ZnO has been successfully performed using a variety of methods including electrochemical deposition\cite{56-61}, RF plasma and magnetron sputtering\cite{43, 60, 62, 63}, ball mill grinding of ZnO and Al₂O₃ powder followed by sintering\cite{53}, pyrolytic and thermal decomposition\cite{64-66}, and laser ablation\cite{44}. Al doping is desirable for many applications, including dye-sensitized solar collectors\cite{60}, thermoelectrics\cite{43, 44, 53, 62}, nanostructures\cite{59}, and light emitting diodes\cite{56}. The moderate bandgap and high electrical conductivity of 2% (molar ratio of Al to Zn) doped Al:ZnO contributes to its excellent thermoelectric performance, while its high thermal conductivity is its greatest detractor for thermoelectric applications\cite{44, 53}. It is an excellent candidate for microstructuring to reduce thermal conductivity.

Aluminum can be integrated into the film using a variety of fabrication techniques\cite{55, 64, 65, 67-69}. The preferred type of integration involves substitution doping of ZnO where zinc ions are replaced by aluminum ions in a predominantly ZnO crystal lattice. The replacement results in localized distortions in the lattice structure and serves as an n-type dopant, in some cases yielding extremely high electrical conductivity exceeding 2000 S/cm\cite{54}. Aluminum has also demonstrated p-type doping effects when co-doped with nitrogen\cite{70}. The ideal methodology for growing Al:ZnO thermoelectrics would

- allow for the introduction of nanostructural features such as voids or heterostructures,
- permit gradient or controlled doping for electronic band tailoring and reducing electronic contribution to thermal conductivity,
- support a rapid rate of growth,
- be scalable to large surface areas,
- and require a minimum of energy to help reduce fabrication costs.

Most methods for fabricating Al:ZnO involve either vacuum deposition or sintering a powder at temperatures above 900°C, both of which demand significant energy and equipment\cite{44, 52, 62}. Hydrothermal and electrochemical (wet) growth of ZnO thin films and nanostructures are both well established in literature and resolve some of these limitations\cite{40, 66}. Growth
of ZnO in solution occurs at low temperatures, is scalable, and provides ample flexibility to modify the properties of the material during growth through the introduction of dopant chemicals and capping agents\cite{40, 58}. Some work has also been performed on growing Al:ZnO thin films electrochemically by adding dopant agents into the growth solution, but the thermoelectric properties of electrochemically grown Al:ZnO have not been investigated\cite{56–59, 61, 65}. Due to the versatility, low cost, and scalability of the electrochemical deposition of Al:ZnO, electrodeposition was chosen as the fabrication methodology for this work.

1.2.4 Electrochemistry

Electrodeposition involves the use of electrochemistry to deposit material onto a substrate. In a standard three electrode configuration, a substrate (cathode) onto which the desired material is to be deposited is connected to a wire and is placed within a solution containing ions. A counter electrode, or anode, is chosen to complete the circuit and allow a site where oxidation can take place. An optional reference electrode is typically included for more accurate measurement of solution potential relative to the substrate. Electrodeposition can occur potentiostatically, where applied potential between anode and cathode is adjusted to maintain a constant reference potential, or galvanostatically, where a constant current between anode and cathode is applied. A basic potentiostatic setup is shown in Figure 1.4. Depositions necessarily operate below the boiling point of the process fluid, typically water, and are historically ubiquitous for plating metals, including aluminum, gold, and chromium\cite{71}. Recent work with electrochemistry has enabled the deposition of more complex materials such as ZnO\cite{72, 73}.

Electrochemistry offers very versatile control of the material formation, permitting variations in solution temperature, applied potential, and solution chemical composition as methods for varying the properties of the films during growth, enabling the formation of a large variety of nanostructures\cite{40, 74}. The anion groups typically used in ZnO electrodeposition are nitrates, sulphates, acetates, and chlorides\cite{72, 73, 75}. Of these anion groups, nitrates and chlorides have been most explored within the literature\cite{72, 73, 76–88}. Depositing ZnO with chloride anions requires the addition of gaseous oxygen to the growth solution to form the oxide, whereas the nitrate anion provides the oxygen through electrochemical decomposition of nitrate into hydroxide as shown by the following reaction\cite{40, 77, 80, 82, 84, 89}:

\[ \text{Zn}^{2+} + \text{NO}_3^- + 2 \text{e}^- \rightarrow \text{ZnO} \downarrow + \text{NO}_2^- \] (1.20)
1.3. Objectives

The overarching objective of the work is to produce a low cost, environmentally friendly n-doped thermoelectric material suitable for integration into a thermoelectric module. This objective is separated into the following tasks:
1.3. Objectives

1. Develop a modelling methodology to rapidly approximate the relative thermal conductivity of similar nanostructures.

2. Use modelling to qualitatively assess the thermal behaviour of nanostructured ZnO and choose structures for experimental synthesis.

3. Synthesize high quality, thick film Al:ZnO with the desired structures using electrochemistry.

4. Test the thermoelectric properties of the synthesized Al:ZnO structures.
Chapter 2

Modelling

There exists a wide range of nanostructures with the potential for synthesis with the Al:ZnO material system that may augment the thermoelectric performance of the material\cite{90, 91}. Since the thermal conductivity of unmodified bulk Al:ZnO is approximately 20-40 W m$^{-1}$ K$^{-1}$ at room temperature\cite{53}, finding nanostructures that reduce lattice thermal conductivity proportionately more than electronic conductivity was the focus of this work. To determine which structures warrant experimental examination, a consistent, primarily qualitative mechanism that takes into account special phonon scattering mechanisms that are difficult to describe through existing analytical theory was developed to enable the rapid comparison of the thermoelectric performance of various nanostructures. To simplify the modelling of the materials, undoped ZnO was used in all simulations. It is assumed that thermoelectrically beneficial nanostructural features will apply similarly to both ZnO and Al:ZnO material systems for low doping densities.

The behaviour of phonons within nanostructured materials has been a subject of intense study using a remarkable variety of numerical and analytical modelling techniques. For example, to model the behaviour of roughness on silicon nanowires, which has experimentally produced a 100× reduction in thermal conductivity\cite{26}, models have been constructed using Monte Carlo simulations\cite{92, 93}, atomistic Green’s function\cite{94–96}, the Boltzmann Transport Equation (BTE)\cite{97, 98}, perturbation theory\cite{99}, scattering-matrices\cite{100}, molecular dynamics\cite{98, 101, 102}, phonon hydrodynamics\cite{103}, and finite element analysis\cite{104}. Others have assembled tools for estimating phonon propagation through nanostructures based on various classical and quantum assumptions\cite{105, 106}. These models are often designed to favour a small subgroup of nanostructures, such as surface roughness features, or they make assumptions about the behaviour of phonons that neglect their wave-like behaviour around nanometre-scaled obstacles\cite{4}.

To minimize the risk of bias in phonon modelling, molecular dynamics was chosen. Molecular dynamics uses either experimentally or theoreti-
cally derived force fields to model the interaction between small subsets of atoms within a large lattice. The simulation runs iteratively with a constant time step, allowing for the natural evolution of phonon behaviour as a mesoscopic culmination of the interactions between all of the atoms in the model. Molecular dynamics has been successful in modelling the behaviour of nanostructures, but it is generally limited in that significant computational resources are required to run the simulations\[101, 107, 108\]. To help provide better insight into the phonon behaviour around nanostructures, a method for rapidly simulating and producing phonon density maps using local vibrational density of states (LVDOS) was developed. LVDOS equilibrium molecular dynamics (LVDOS-EMD) simulations could also provide relative thermal conductivities between similar nanostructures, enabling the study and comparison of many different structures using significantly fewer resources.

All thermal conductivity modelling was performed assuming a system at 300 K. This temperature was selected for many reasons: 1) The cold side of a thermoelectric device will be near this temperature in most applications; 2) The force field chosen for modelling ZnO, ReaxFF, was characterized at this temperature\[109\]; 3) At 300 K, calculated vibrational (occupied) density of states will closely match material density of states; 4) Temperatures above 600 K would prevent studying the Zn/ZnO heterostructure.

ZnO is a very stable material over a wide range of temperatures and experimentally demonstrates good adherence to the Callaway model for lattice thermal conductivity\[16, 110\]. It is therefore assumed that reductions in thermal conductivity at room temperature will lead to corresponding reductions in thermal conductivity at all temperatures. No nanostructures were chosen specifically to create temperature-dependent phonon interference patterns, although such structures do exist\[111\]. The effect of the aluminum dopant was also neglected in the models as each model was expected to be doped identically, and dopants provide defect scattering sites which are expected to reduce thermal conductivity in all cases.

Of the variety of nanostructures available, unmodified nanowires, hollow nanowires\[40\], surface roughened nanowires\[112\], nanovoided bulk\[31, 32\], and superlattice nanowires\[113, 114\] were chosen for primary investigation through modelling. Some additional structures were briefly considered for their viability as well, such as zinc-filled ZnO tubes, but were found to be chemically unstable and were thus not explored in further detail.
2.1 LVDOS-EMD

This section discusses the methods used for determining thermal conductivity of silicon and ZnO nanostructures, including the development of local density of states equilibrium molecular dynamics (LVDOS-EMD). The methodology is first illustrated using silicon due to the comparatively rapid MD simulation of silicon over ZnO and its well established force fields for thermal conductivity calculation.

Thermal conductivity in an anisotropic material can be defined using Fourier’s equation

\[ Q = -\kappa \nabla T, \]

where \( Q \) is the heat flux vector, \( \kappa \) is the thermal conductivity tensor, and \( \nabla T \) is the temperature gradient. \( \kappa \) includes the effects of both electrons and phonons, where the former can generally be neglected in high thermal conductivity (>20 W m\(^{-1}\) K\(^{-1}\)) dielectric and semiconducting materials. Assuming no radiative transfer, heat transfer occurs primarily through lattice vibrations in wavelets called phonons.

Several means exist for using molecular dynamics (MD) for determining the thermal conductivity of a nanostructured material. Most commonly, MD simulations using equilibrium molecular dynamics (EMD) and non-equilibrium molecular dynamics (NEMD) are performed. Molecular dynamics discretely simulates the motion of a collection of atoms under specified conditions based on pre-calculated or empirically determined potentials. EMD simulations using methods such as Green-Kubo involve relaxing the atomic structure under study at thermal equilibrium [115, 116]. In Green-Kubo, correlations are used to examine the decay of coherent phonon wavelets as they traverse the structure[117]. Simulations must typically execute > 1 × 10\(^6\) iterations depending on the material thermal conductivity, and multiple simulations must be executed and the results averaged to converge at a reasonable thermal conductivity[118]. This method is useful for determining the thermal conductivity of a material at a specified temperature and is often used to estimate thermal conductivity in many directions concurrently. Substantial computing time is required to execute the simulations, and they may not converge if the structure is complex with many interstitial and surface features[119, 119, 120].

Reverse NEMD (herein also referred to simply as NEMD) involves inducing a thermal flux within the material by swapping kinetic energy and momentum between two groups of atoms. The Mueller-Plathe (MP), a direct method, swaps the energy and momentum of the hottest atom in the
2.1. **LVDOS-EMD**

“cold” region and the coolest atom in the “hot” region thereby gradually forming a temperature gradient between “hot” and “cold” regions [107, 121]. Once the gradient reaches steady state, the energy flux and temperature gradient across the structure are both acquired and used to determine the thermal conductivity. This method has a high probability of success for stable structures, but it is also limited by requiring many execution steps ($>1 \times 10^6$ iterations), large structures to accommodate all relevant phonon wavelengths [111, 122], and a thermal gradient disallowing equilibrium thermal conductivity calculations. Preliminary simulations are also required in setting up the model to determine an appropriate energy transfer rate to achieve the desired temperature gradient.

Another method, homogeneous non-equilibrium molecular dynamics (HNEMD), provides a variation of NEMD that is significantly more computationally efficient by using linear response theory along with a mechanical analog of the thermal transport process to calculate transport coefficients [123]. HNEMD leverages information from the force field potentials used in the MD simulation and can provide results of comparable accuracy to Green-Kubo with an order of magnitude fewer computations, but requires several simulations to determine an appropriate range of simulation constants [124]. HNEMD is very material-specific and must be properly configured for both the material system and potential to yield meaningful results, but with recent support for multiple material systems, it is a promising methodology for the analysis of nanostructural features.

A subclass of methods for determining $\kappa$ that depend on EMD or NEMD results involves a combination of lattice dynamics calculations and the Boltzmann transport equation (BTE). For an isotropic, periodic solid with $n$ atoms per unit cell, the phononic BTE along a specific material direction is [125]

$$\kappa = \sum_s \int_q v_g^2(q, m) C(q, m) \tau(q, m) dq,$$

where $v_g(q, m)$ is the phonon group velocity, $C(q, m)$ is the mode heat capacity, $\tau(q, m)$ is the phonon lifetime, $q$ refers to the phonon wavevector, and $m$ is the phonon mode [125]. The heat capacity can be calculated using the temperature derivative of the Bose-Einstein distribution directly from the mode information, meaning that group velocity and phonon lifetime must be determined from the modelling results. A typical approach involves first solving the dynamical matrix of the system after minimizing the system energy through a relaxation procedure under NPT conditions. The eigenvec-
tors can then be used to calculate group velocity as described by McGaughey and Larkin\cite{126}. Several methods exist for then determining phonon lifetime, including normal mode decomposition (NMD)\cite{126}, first principles molecular dynamics\cite{125}, and spectral energy density calculations\cite{127}. All of these methods operate within reciprocal or phonon space, requiring the computationally intensive task of determining phonon modes from a dynamical matrix calculation and/or modelling results.

LVDOS-EMD is applied to both EMD and NEMD (LVDOS-NEMD) simulation environments developed herein can be applied in both EMD and NEMD simulations and uses local vibrational density of states (LVDOS) combined with the Boltzmann Transport Equation (BTE) to calculate the relative thermal conductivity between multiple similar structures, such as structures with varying densities of defects, or varied surface morphology. The methodology, herein called LVDOS-EMD, requires very few computing cycles at equilibrium and is targeted toward examining the effect of progressive, small nanostructural modifications on material thermal properties at identical temperatures. It is primarily intended for qualitatively supporting more rigorous EMD and NEMD methods by determining trends and patterns, and is not intended to provide an absolute thermal conductivity. By operating within real space using simulated velocity data, insights into localized wave behaviour around nanostructural features can be realized. It is demonstrated using notched, square silicon nanowires and is compared to NEMD MP and finite element analysis (FEA) results. FEA results are included to highlight the importance of including wave effects over classical continuum heat transfer models.

Nanowire roughness is represented by notches of various depths ($D$), periods ($p$), and widths ($w$) to create regions of differing VDOS and MFP as shown in Figure 2.1. Tests are performed on nanowires of various thicknesses ($k$). Silicon nanowires are first used to aid in validating the theory due to their ease of simulation and well established force fields for thermal conductivity calculations. Simulating the thermal conductivity of ZnO has few rigorously examined force fields available and little established literature on simulating thermal properties\cite{109, 128, 130}.

2.1.1 Formulation of Theory

2.1.1.1 Boltzmann Transport Equation

Following the derivation of Grimvall, the quantum statistical BTE for vibrations in real space is used to provide an equation for thermal conductivity
2.1. LVDOS-EMD

Figure 2.1: A visual representation of a Si lattice structure showing roughening parameters is shown. This figure shows the structure prior to relaxation and is intended to highlight the parameters varied in the notching in advance of executing the simulation. Nanowires are structured along the \langle 001 \rangle direction.

\[ \kappa_{\text{vib}} = \frac{N}{3V} v_g \int_{0}^{\omega_{\text{max}}} C_{\text{vib}}(\omega) l(\omega) D(\omega) d\omega, \]  

where \( N \) is the number of particles in the system, \( V \) is the total volume, \( \omega \) is the vibrational frequency, \( v_g \) is the average wavelet group velocity, \( l(\omega) \) is the mean free path (MFP), \( D(\omega) \) is the vibrational density of states (VDOS), and \( C_{\text{vib}}(\omega) \) is the heat capacity, which, using the temperature derivative of the Bose-Einstein distribution, can be expressed as \[ C_{\text{vib}}(\omega) = k_B \frac{y^2 e^y}{(e^y - 1)^2}, \]

where

\[ y = \frac{\hbar \omega}{k_B T}. \]

Appropriate normalization for calculating thermal conductivity requires that

\[ \int_{0}^{\infty} D(\omega) d\omega = 3. \]
2.1. LVDOS-EMD

conductivities between two similar nanostructured materials,\[
\frac{\kappa_{vib,1}}{\kappa_{vib,2}} = \frac{\int_{0}^{\omega_{\text{max}}} C_{vib}(\omega) l_1(\omega) D_1(\omega) d\omega}{\int_{0}^{\omega_{\text{max}}} C_{vib}(\omega) l_2(\omega) D_2(\omega) d\omega},
\]
where \(l_i(\omega)\) and \(D_i(\omega)\) represent the MFP and VDOS of each structure, \(i\). An MD simulation using a more rigorous methodology, such as Green-Kubo or Mueller-Plathe, is run on a reference structure to determine its MFP, VDOS, and \(\kappa_{vib}\). The relative thermal conductivity of other, similar structures, can then be calculated using the reference structure as a scaling factor. After the rigorous simulation is complete, two variables per similar structure must be solved: 1) The VDOS and 2) the frequency-dependent mean free path.

2.1.1.2 Vibrational Density of States

Real space VDOS can be calculated from MD simulations using the velocity autocorrelation function (VAF) on aggregates of atoms [132, 133]. If the velocity vector of atom \(a\) is \(v_a(t)\) then the VAF, \(Z_a(t)\), can be written as
\[
Z_a(t) = \frac{\langle v_a(0) \cdot v_a(t) \rangle}{\langle v_a(0) \cdot v_a(0) \rangle},
\]  
where \(v_a(0)\) represents the velocity at the beginning of the captured data \((t = 0)\) after the system has reached equilibrium. The frequency spectrum can be determined through the application of a Fourier transform,
\[
F_a(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-i\omega t} Z_a(t) dt,
\]
resulting in a discretized, VDOS of
\[
D(\omega) = \sum_a F_a(\omega) F_a^*(\omega).
\]

Morphological changes in nanostructured materials along the path travelled by vibrational energy can significantly change the VDOS by anharmonic collisions. These shifts can be significant, causing order of magnitude changes in thermal conductivity [134]. When examining the VDOS of the structure as an aggregate whole, the influence of small structural features can be lost, leading to large errors in the calculated thermal conductivity. It is for this reason that local vibrational density of states is used for both VDOS and MFP calculations.
2.1. LVDOS-EMD

The structure is separated into segments of equal volume such that each segment has a minimum of 50 atoms and the segments are stacked along the direction of measurement. The segment length should be selected to avoid correlation with surface features and minimize the variation in number of atoms between adjoining segments. Ideal segment length is typically related to material lattice parameters to ensure an even distribution of atoms. The VDOS is calculated separately for each segment, providing localized density of states throughout the structure. An example of the VDOS for a 4.9 nm diameter silicon nanowire is shown in Figure 2.2. Shown are spatially localized vibrational components of optical and acoustic phonons along the length (z-axis) of both straight and notched nanowires with the band spreading effects of the notching visible in Figure 2.2b.

Calculating the LVDOS for each segment is based on (2.10) where

\[
D_s(\omega) = \sum_a F_{a,s}(\omega) F_{a,s}^*(\omega) \tag{2.11}
\]

is the aggregate LVDOS for a segment or slice, \(s\), of the nanostructure(s) along the direction of measurement. A cross-sectional area that encompasses the largest necessary cross-section for the structure must be selected for the segments. The cross-sectional area and the width of each segment must be identical. The LVDOS of each segment cannot be normalized by the number of atoms in the segment, meaning that the segment size should be selected to minimize the variation in total atoms between segments.

Determining an approximate mean free path using only the LVDOS begins with a discretization and modification of the survival equation.

2.1.1.3 Survival Equation

In the derivation of the survival equation for determining the mean free path of a particle travelling through a random collection of identical particles within a defined volume (a gas), the gas is first segmented into a series of volumes and the particle is represented as a bullet as shown in Figure 2.3. The following derivation follows Sears\textsuperscript{[135]}. The probability of a bullet striking a particle while travelling through a segment is

\[
\frac{\Delta N}{N} = \frac{\text{Target area}}{\text{Total area}}, \tag{2.12}
\]

where \(N\) is the total number of travelling bullets (or density of bullets) and \(\Delta N\) is the number of collisions\textsuperscript{[135]}. If \(A\) represents the cross-sectional area
2.1. LVDOS-EMD

Figure 2.2: LVDOS along the $z$-axis of a $4.9 \times 4.9 \times 27\text{nm}^3$ (a) straight and (b) notched silicon nanowire. The roughened nanowire in (b) has 1.6 nm deep, 0.54 nm diameter notches every 5.4 nm along its length. Slices were made every 0.135 nm along the nanowire and are labeled along the $x$-axis.
of the targets and \( n \) is the number of targets per unit volume then

\[
\frac{dN}{N} = -nAdx
\]  

(2.13)

From (2.13), if every slice is assumed to be identical then the survival equation,

\[
N = N_0 e^{-nAx},
\]  

(2.14)

is determined to be a decaying exponential function where \( N_0 \) is the total number of bullets at the origin. Mean free path is then a normalized weighted average of the number of bullet collisions travelling through an infinite distance,

\[
l = \frac{\sum x\Delta N}{N_0} = nA \int_0^\infty xe^{-nAx}dx = \frac{1}{nA}.
\]  

(2.15)

In the original kinetic theory of gasses derivation of the mean free path, the assumption is made that successive layers or segments of target atoms occupy the same configuration, meaning that the probability of a collision as a particle travels through a material is identical per unit distance [135]. A variation on this derivation is proposed. Rather than treating the probability of collision as a function of “microscopic collision cross-section” and
“target area”, the probability of a collision is approximated by the change in VDOS between neighbouring segments. When wavepackets travel from a region with many states to a region with fewer states, some collisions are statistically required. For wavelets moving in a single direction, from segment $s - 1$ to $s$, and for small $\delta x$, if the transition from a region of high occupied DOS to a region of low occupied DOS is large, then an approximate survival probability, $Z_s$, can be derived by considering the ratio in occupied vibrational density of states, $N$, between the two regions,

$$Z_s \approx \frac{N_s}{N_{s-1}} \text{ for } N_s < N_{s-1}. \quad (2.16)$$

If we then assume that the probability of a wavelet colliding is identical for all wavelets, the probability of collision from wavelets travelling from a region of low density to high density can be approximated from wavelets travelling in the opposite direction using the same principles as (2.16),

$$Z_s \approx \frac{N_{s-1}}{N_s} \text{ for } N_{s-1} < N_s. \quad (2.17)$$

Equations (2.16) and (2.17) represent the maximum probability of survival of wavelets travelling through these spaces. A more rigorous model considering wavelets travelling in both directions for a single mode can be constructed beginning with the principal statement of the Boltzmann Transport Equation (BTE),

$$\frac{\delta N_s}{\delta t} = \frac{\delta N_s}{\delta t}_{force} + \frac{\delta N_s}{\delta t}_{diff} + \frac{\delta N_s}{\delta t}_{coll}, \quad (2.18)$$

describing the time varying change in density of states as a summation of force, diffusion, and collision influences for every segment, $s$. Assuming that the system is in equilibrium and that no force is applied, (2.18) becomes

$$0 = \frac{\delta N_s}{\delta t}_{scatt-in} - \frac{\delta N_s}{\delta t}_{scatt-out} + \frac{\delta N_s}{\delta t}_{diff-in} - \frac{\delta N_s}{\delta t}_{diff-out}, \quad (2.19)$$

where scattering terms represent interactions with wavelets in the same segment but in different modes, and diffusion terms represent wavelets in the same mode entering and leaving the segment from neighbouring segments. Wavelets can arrive by travelling into the segment from a neighbouring
2.1. LVDOS-EMD

segment or by scattering in from a different mode in the same segment. Wavelets depart either by travelling out of the segment ballistically or by interacting anharmonically and scattering to a different mode within the same segment. This equation can also be understood as an expression of conservation of energy. For a system where \( N_{s-1} > N_s \) and \( N_{s+1} > N_s \),

\[
\frac{\delta N_s}{\delta t} |_{\text{scatt-in}} = \zeta N_s, \tag{2.20}
\]

\[
\frac{\delta N_s}{\delta t} |_{\text{diff-in}} = \beta N_{s-1} + \beta N_{s+1}, \tag{2.21}
\]

\[
\frac{\delta N_s}{\delta t} |_{\text{scatt-out}} = (1 - Z_s) \left[ \frac{\delta N_s}{\delta t} |_{\text{diff-in}} + \frac{\delta N_s}{\delta t} |_{\text{scatt-in}} \right], \tag{2.22}
\]

\[
(1 - Z_s) \zeta N_s + (1 - Z_s) \beta N_{s-1} + (1 - Z_s) \beta N_{s+1},
\]

\[
\frac{\delta N_s}{\delta t} |_{\text{diff-out}} = 2 \beta N_s, \tag{2.23}
\]

where \( \beta \) represents the proportional rate of wavelets in the same mode entering or leaving the segment due to diffusion, \( \zeta \) is the proportional rate of wavelets scattering into the segment from other modes, and \( N_{s-1} \) and \( N_{s+1} \) represent the LVDOS adjacent to each segment boundary, as shown in Figure 2.4. The scattering out term applies to all wavelets entering the segment per unit time. Survivability, \( Z_s \), is not a time-dependent term and is applied only once to wavelets as they enter the segment. All wavelets within segment \( s \) are assumed to have the same probability of collision, including wavelets that have scattered into the mode. All wavelets that collide scatter out to a neighbouring mode within the same segment. Combining (2.20)-(2.23) with (2.19) yields

\[
Z_s = \frac{2 \beta N_s}{\beta(\frac{\zeta N_s}{\beta} + N_{s-1} + N_{s+1})} \tag{2.24}
\]

for \( N_{s-1} > N_s, N_{s+1} > N_s \).

The \( \beta \) terms are analogous to the group velocity of the system, which is taken to be identical for wavelets entering and leaving each segment due
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Figure 2.4: Illustration of the transport of wavelets within a multi-segmented structure, where red particles are travelling within the same mode along the structure, and blue particles originate from intermode scattering in the same segment.

to diffusion. Similar to (2.16) and (2.17), (2.24) represents the maximum survivability of wavelets travelling through the segment. Provided that the material MFP is defined predominantly by structural features in the material, we assume that $\beta >> \zeta$. The resulting equation is the approximate probability of survival for each segment,

$$Z_s = \frac{2N_s}{N_{s-1} + N_{s+1}}$$  \hspace{1cm} (2.25)

for $N_{s-1} > N_s, N_{s+1} > N_s$.

The equations for the other neighbour configurations of $N_s$ are determined similarly to (2.16) and (2.17), yielding

$$Z_s = \frac{N_s + N_{s+1}}{N_s + N_{s-1}}$$  \hspace{1cm} (2.26)

for $N_{s-1} > N_s, N_{s+1} < N_s$,

$$Z_s = \frac{N_s + N_{s-1}}{N_s + N_{s+1}}$$  \hspace{1cm} (2.27)

for $N_{s-1} < N_s, N_{s+1} > N_s$. 27
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\[ Z_s = \frac{N_{s-1} + N_{s+1}}{2N_s} \]  \hspace{1cm} (2.28)

for \( N_{s-1} < N_s, N_{s+1} < N_s \).

2.1.1.4 Determination of Mean Free Path

The frequency dependent MFP can now be determined from MD results through a weighted average of collision probabilities across all segment boundaries. Equations (2.25)-(2.28) can be described in terms of LVDOS and vibrational frequency as

\[ P_s(\omega) = \frac{2D_s(\omega)}{D(\omega)_{s-1} + D(\omega)_{s+1}} \]  \hspace{1cm} (2.29)

for \( D(\omega)_{s-1} > D(\omega)_s, D(\omega)_{s+1} > D(\omega)_s \),

\[ P_s(\omega) = \frac{D(\omega)_s + D(\omega)_{s+1}}{D(\omega)_s + D(\omega)_{s-1}} \]  \hspace{1cm} (2.30)

for \( D(\omega)_{s-1} > D(\omega)_s, D(\omega)_{s+1} < D(\omega)_s \),

\[ P_s(\omega) = \frac{D(\omega)_{s-1} + D(\omega)_{s+1}}{2D(\omega)_s} \]  \hspace{1cm} (2.31)

for \( D(\omega)_{s-1} < D(\omega)_s, D(\omega)_{s+1} > D(\omega)_s \),

\[ P_s(\omega) = \frac{D(\omega)_{s-1} + D(\omega)_{s+1}}{2D(\omega)_{s-1}} \]  \hspace{1cm} (2.32)

for \( D(\omega)_{s-1} < D(\omega)_s, D(\omega)_{s+1} < D(\omega)_s \),

where \( P_s(\omega) \) is the wavelet probability of survival travelling through segment \( s \) such that \( P_0(\omega) = 1 \), and \( D_s(\omega) \) represents the cumulative, frequency dependent LVDOS of a segment and is determined using (2.11). With the probability of survival calculated for every segment, the probability of a localized wave surviving exactly \( s \) segments, \( Q_s(\omega) \), is

\[ Q_s(\omega) = \left[ 1 - P_s(\omega) \right] P_0(\omega) P_1(\omega) P_2(\omega) ... P_{s-1}(\omega) \]  \hspace{1cm} (2.33)

\[ \left[ 1 - P_0(\omega) \right] \prod_{y=0}^{s-1} P_y(\omega) \] .

The distance traveled, \( d_s \), is simply

\[ d_s = sa, \]  \hspace{1cm} (2.34)
where $a$ is the length of each segment, which is taken to be identical for all segments, and $s$ is the segment index such that the product $sa$ is the total distance travel from the origin ($s = 0$) to $d_s$. Combining the probability of particle survival from (2.33) and distance traveled for all segments yields the approximated frequency dependent MFP,

$$l(\omega) \approx a \sum_{s=1}^{S} [s(1 - P_s(\omega)) \prod_{y=0}^{s-1} P_y(\omega)],$$

(2.35)

where $S$ is the total number of segments.

### 2.1.2 Validation of Theory

The validity of (2.35) is first examined using a Monte Carlo simulation that uses particles to approximate wavelets. These particles traverse a one-dimensional medium that follows simple rules defined by (2.20)-(2.23). The simulation is used to determine whether the non-frequency dependent equivalent of (2.35) can be used to determine the MFP of particles in a simple system using only the measured number of particles in neighbouring segments. Following the Monte Carlo simulation, the dynamical matrix is solved for some of the nanostructured unit cells used in the MD simulations. VAF-based VDOS using MD results is compared with the DOS calculated using only the normal modes from the dynamical matrix of the system. The group velocities of various structures are calculated and compared to examine the effect of small structural changes, and normal mode decomposition is used to calculate phonon lifetime and conceptual MFP for comparison with LVDOS-EMD results. Straight nanowires and phonon VDOS variation over the entire sampling period are also considered.

LVDOS-EMD molecular dynamics data was generated using plain and roughened silicon nanowires ranging from 1.6 nm to 4.9 nm diameter and were all 217.2 nm (400 unit cells) long. The selection of this length is discussed in Section 2.1.3. The software used was LAMMPS with the Stillinger-Weber potential [136]. The Stillinger-Weber potential has been previously demonstrated to accurately model the thermal properties of silicon [136, 137]. All simulations began by applying a Gaussian velocity profile to all atoms representing an aggregate temperature of 300 K. This step was followed by 50,000 iterations at 1.0 fs of simulation time per iteration of constant number of particles, pressure, and temperature (NPT) equilibration. A constant number of particles, volume, and energy (NVE) equilibration for 25,000 iterations was then used to allow any temperature transients in
the system to settle. At this stage, either Mueller-Plathe was applied for a reverse NEMD simulation or LVDOS-EMD was applied for a short duration simulation. Stabilization of a thermal gradient for reverse NEMD calculations then required 1,000,000 iterations, followed by 200,000 iterations for collecting temperature and flux data for calculating the thermal conductivity. The final mean temperature of the entire nanowire was measured to confirm 300 ± 5 K to ensure that each simulation properly equilibrated. The structures were also studied after simulation to ensure that no atoms were lost and that the nanowire remained straight throughout the simulation.

2.1.2.1 Monte Carlo Simulation

A stochastic Monte Carlo computational simulation was developed to determine the accuracy of (2.35) in an ideal system. Particles representing wavelets in a single mode were initially generated and placed along a segmented, one-dimensional axis representing a structure analogous to a nanowire. The simulation used (2.20) - (2.23) to determine particle creation and destruction behaviour, where \( Z \) was predetermined for each segment in the simulation. Each particle starting location, speed, and direction were randomly determined using a uniform distribution function. Particle positions were updated over several thousand simulated time steps and localized, instantaneous particle density was calculated for each segment with every time step. Each segment along the “nanowire” was assigned a survival probability from 10 - 100\%, representing the probability of particles colliding upon entering the segment, simulating scattering due to collisions. This probability is analogous to physical structural features such as holes or notches that increase phonon scattering along a nanostructured material. Scattered particles were replaced with a new particle at a random location along the nanowire with particle density in each segment proportional to the relative probability of the particle appearing in that segment. The number of particles in motion was set to be constant for every time step. Particle mean free path was measured directly for each particle then averaged over several hundred thousand particles to determine the measured mean free path. To improve the accuracy of the simulation, the number of particles in each segment was summed with each time step to represent the large number of samples required to perform a Fourier transform in a physical simulation. Analysis was only performed on the summed particle occupation data.

A periodic structure was first modelled with segments of high collisions and low collisions to represent an inhomogenous, nanostructured material. Particle survivability in high collision segments was varied from 10 - 80\%.
over eight simulations. The resulting cumulative particle density over 2,000 simulation time steps for a configuration where every 10 segments was assigned an 80% survival probability is shown in Figure 2.5 as an example. The figure shows that regions of 100% survivability have a similar, but random number of accumulated particles in each, and regions of 80% survivability have a correspondingly lower number of total particles due to collisions removing particles from those segments throughout the simulation. Similar simulations were also conducted where 80% survivability was replaced with lower values.

Figure 2.5: A plot of the cumulative particle density across 200 segments of a 1,000 segment structure where each segment has a 100% survival rate except for each 10th segment, which has an 80% survival rate. The simulation assumes an instantaneous particle density expectation value of 10 particles/segment and runs over 2,000 simulation time steps.

Equation 2.35 provides an approximate MFP along one dimension exclusively using the calculated cumulative LVDOS of the structure over a specified time interval. Analyzing VDOS at a moment in time is not possible as the Fourier transform must take place over a range of time steps. Figure 2.6 demonstrates the resulting calculated MFPs as a function of simulation time window duration. The rapid convergence indicates that in an idealized model, the MFP is independent of sampling time window provided a minimum window size is met. This minimum is necessary for the system to reach equilibrium as required by (2.19). Deviations in Figure 2.6 from the
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converged MFP early in the simulation are the result of the model establishing an equilibrium where the regions of lower survivability converge to the appropriate density shown in Figure 2.5. Vibrations travelling through a real structure must also demonstrate the same behaviour for LVDOS-EMD to be applied successfully. Discussion of VDOS as a function of sampling window size can be found in Section 2.1.2.6 and demonstrates a similar consistency provided a minimum sample window size and VDOS are met.

![Figure 2.6: Calculated MFP as a function of time window size using (2.35) applied to simulations with segments of 10% survivability (lowest curve) through 80% survivability (highest curve).](image)

Figure 2.6 shows the simulation results with a constant simulation time window size of 2000. In addition to comparing the correct MFP by tracking particle travel distance and MFP calculated as described above, a variation on (2.16)-(2.17) was considered where the mean of all three DOS terms are used in the denominator. Using the mean represents the average survival at boundaries \( N \) and \( N_{s-1} \) rather than the minimum. Although using the mean particle density of the two adjacent segments does provide a better match to the measured density for regions of greater survivability, using the maximum DOS between neighbouring regions, represented by the equations as presented, provides a more consistent approximation across the entire range. Using equations (2.25) - (2.28) produced nearly identical results.
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2.1.2.2 Lattice Dynamics Density of States

Lattice dynamics involves determining the permissible phonon modes in k-space by forming and solving a discretized dynamical matrix that captures the force interactions between atoms in a structure. Studying the behaviour of phonons should provide an analogous reference to the vibrational wavelets that are the focus of LVDOS-EMD. A full discussion of lattice dynamics and normal mode decomposition can be found elsewhere[126]. The dynamical matrix can be used in the eigenvalue problem,

\[ \omega(q,m)^2 e(q,m) = D(q)e(q,m), \]  

where \( \omega(q,m) \) is the phonon mode-dependent angular frequency, \( e(q,m) \) is the eigenvector matrix, and \( D(q) \) is the dynamical matrix. There are three modes per atom, and the dynamical matrix scales with number of modes squared, requiring significant computational resources to solve very large systems of atoms. Calculations herein used the Stillinger-Weber potential and the GULP software package to generate the dynamical matrix based on a provided structure and create the corresponding eigenvectors and VDOS[136, 138]. GULP was configured to optimize the structure first, then generate the full dynamical matrix and perform phonon calculations.
Matrices were generated at 300 K using the smallest possible unit cell that could periodically replicate the desired nanostructure. Thirty k-points were used along the \( \langle 001 \rangle \) axis for each structure studied. A custom Matlab script then loaded the output data from GULP to perform further calculations.

Total phonon density of states was produced using GULP lattice dynamics for 2.7 nm and 3.8 nm diameter straight and notched nanowires, and was compared with the VDOS generated using MD and VAF for the identical structures. The results are shown in Figure 2.8. There is excellent agreement between the straight nanowires calculated using both techniques, but the VDOS using VAF generated for the notched nanowire diverges from the theoretical ideal. Although acoustic phonons match well in all data sets, optical phonons are not as prominent in the MD data. The error is likely caused by dangling silicon bonds in the MD simulation warping the structure of the nanowire around the notches, modifying the dispersion and corresponding VDOS of the structure. It is also possible that some available, high energy optical states were not filled by phonons due to very short phonon lifetimes and the finite temperature of the chosen structure. The LVDOS-EMD method assumes that all available states are filled, so structures with significantly different VDOS may have higher error.

![Figure 2.8: The vibrational density of states calculated using VAF for a 2.7 nm (5 unit cells) diameter silicon nanowire notched every two unit cells and a 3.8 nm straight nanowire, and the total phonon density of states calculated using a dynamical matrix for a similar \( \langle 001 \rangle \) periodic 2.7 nm diameter straight nanowire.](image-url)
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2.1.2.3 Lattice Dynamics Group Velocity

The group velocity can be calculated using the dispersion relation directly [126],

\[ v_g(q, m) = \frac{\delta \omega(q, m)}{\delta q}, \]  

(2.37)

or using the dynamical matrix,

\[ v_{g,i}(q, m) = \frac{1}{2\omega(q, m)} \left[ e^\dagger(q, m) \frac{\delta D(q)}{\delta q_i} e(q, m) \right], \]  

(2.38)

where \( e^\dagger(q, m) \) is the transpose conjugate of \( e(q, m) \).

Both methods were used and with the exception of near the gamma point of the material where the second method yielded an erroneously high group velocity, the results were interchangeable. Group velocity was calculated for straight and notched structures, as shown in Figure 2.9. The results for the various structures examined are very similar, which is necessary for LVDOS-EMD as group velocity cannot be easily calculated directly from MD results. The group velocity does vary significantly across the vibrational spectrum, which can cause error in the LVDOS-EMD calculation if \( v_g \) is taken to a constant independent of vibrational frequency as shown in (2.3), but provided that the structural changes in material equally affect the MFP for all frequencies, the error is less than 5%. Nanostructured systems designed to affect the vibrational mean free path differently depending on the wavelet frequency should use a frequency-dependent \( v_g(\omega) \). It can be calculated for a similar, simpler unit cell to determine the spectral weighting of the velocity, which can then be applied as part of the frequency integration in (2.3).

2.1.2.4 Normal Mode Decomposition

This section follows the derivation of normal mode decomposition discussed by McGaughey and Larkin [126]. Normal mode decomposition combines atom displacements and velocities from molecular dynamics results with the eigenvector normal modes determined through lattice dynamics. By overlaying normal modes onto MD results and studying energy dispersion over time using an autocorrelation function, it is possible to approximate phonon lifetimes for all modes. Although phonons are non-localized within a structure, combining the lifetime with group velocity from lattice dynamics can
produce a hypothetical mean free path that can be compared with LVDOS-EMD results of the same MD simulation[126]. Atoms from lattice dynamics calculations and MD calculations were matched using a least squares minimization and manual adjustment after simulation.

The first step produces the normal mode coordinates and time derivatives, $b(q, m; t)$ and $\dot{b}(q, m; t)$, respectively, using MD and lattice dynamics results using
\begin{equation}
   b(q, m; t) = \sum_{i,j} \left( \frac{M_i}{N} \right)^{1/2} e^{i k \cdot r_0(j)} e_i^*(q, m) \cdot u(j, i; t), \tag{2.39}
\end{equation}
\begin{equation}
   \dot{b}(q, m; t) = \sum_{i,j} \left( \frac{M_i}{N} \right)^{1/2} e^{i k \cdot r_0(j)} e_i^*(q, m) \cdot v(j, i; t), \tag{2.40}
\end{equation}
where $i$ is an iterator for all atoms, $j$ is an iterator for all unit cells, $M$ is atomic mass, $r_0(j)$ is the initial position of the unit cell, and $u(j, i; t)$ is the displacement of the atom from its mean average position. With these values calculated, the potential energy, $U(q, m; t)$, kinetic energy, $T(q, m; t)$, and
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total energy, $E(q, m; t)$, can be calculated using

$$U(q, m; t) = \frac{1}{2} \omega(q, m)^2 b^*(q, m; t)b(q, m; t),$$  \hfill (2.41)

$$T(q, m; t) = \dot{b}^*(q, m; t)\dot{b}(q, m; t),$$  \hfill (2.42)

$$E(q, m; t) = U(q, m; t) + T(q, m; t).$$  \hfill (2.43)

The normalized autocorrelation function of the energy term can then be determined for each mode to produce a decaying oscillation that can be related directly to the phonon mode lifetime, $\tau(q, m)$, such that

$$\langle E(q, m; t) \cdot E(q, m; 0) \rangle / \langle E(q, m; 0) \cdot E(q, m; 0) \rangle = e^{-t/\tau(q, m)}. \hfill (2.44)$$

A simplified means establishing a fit for calculating $\tau$ involves integrating the autocorrelation through all time, or until the function decays to zero,

$$\tau(q, m) \approx \int_0^\infty \frac{\langle E(q, m; t) \cdot E(q, m; 0) \rangle}{\langle E(q, m; 0) \cdot E(q, m; 0) \rangle} dt, \hfill (2.45)$$

and the mean free path can then be determined using

$$l(q, m) = |v_g(q, m)|\tau(q, m). \hfill (2.46)$$

NMD was applied to a 2.7 nm (5 unit cells) nanowire notched every two unit cells and the resulting MFP was compared to results from LVDOS-EMD simulations, shown in Figure 2.10. The MFP produced using the NMD composition produces an output of similar magnitude as LVDOS-EMD, particularly in the low frequency, acoustic band region which significantly contributes to material thermal conductivity. Where discrepancy exists, the LDOS of the vibrational frequency is low, increasing the error of LVDOS-EMD calculations. There is also some discrepancy in the optical phonon spectrum, but this is expected as vibrational occupation in that band differs between the MD results and lattice dynamics results as discussed in Section 2.1.2.2. Other MFP calculations performed for straight, silicon nanowires using LVDOS-EMD, shown in Figure 2.11 produced shapes more consistent with the NMD MFP shown in Figure 2.10.
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![Figure 2.10](image)

Figure 2.10: The vibrational wavelet mean free path calculated using LVDOS-EMD of a 2.7 nm (5 unit cells) silicon nanowire notched every two unit cells is shown and compared with the phonon mean free path of an identical structure calculated using normal mode decomposition.

2.1.2.5 LVDOS of Straight Segments

LVDOS-EMD involves collecting velocity data over a long period in time where vibrations travel throughout the structure potentially impacting the LVDOS of each segment. In an idealized, large, periodic material lacking any nanostructuring, one would expect little or no variation between adjacent slices which would be interpreted by LVDOS-EMD as a system with no collisions. In this section, the impact of sampling window size on the results are considered, as are the variations in LVDOS over time.

In an ideal, conceptual, isotropic material lacking any nanostructural features, summing LVDOS segments over multiple time samples would reduce the variability between segment totals to produce an LVDOS that is essentially identical for every segment. One might also expect this behaviour in a straight nanowire, however this is expected to lead LVDOS-EMD to produce an MFP bounded only by the structure’s simulation length rather than phonon collision behaviour. However, simulations of multiple nanowires in different configurations and widths have yielded reasonable MFPs consistent over multiple simulations with different starting conditions. The MFPs also scale with nanowire diameter, as shown in Figure 2.11.

The behaviour observed in simulated, straight nanowires that explains
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Figure 2.11: MFP calculated using LVDOS-EMD for straight, silicon nanowires from 1.6 nm to 4.9 nm in width. The MFP displayed represents the mean average and standard deviation of all calculated spectral components from 0 - 25 THz for each width.

the success of the algorithm is the formation and temporary persistence of localized regions of high and low vibrational activity. Throughout each structure tested, regardless of nanostructuring, LVDOS varied slowly in each segment, providing variations that could be used normally by the LVDOS-EMD algorithm to approximate a finite MFP. Examples of these regional variations can be seen in Figure 2.2 and Figure 2.14 as changes in colour along the nanowire in each band. Careful analysis of the behaviour of these regions have shown that they can persist for over 50 ps, which is sufficiently long to apply the LVDOS-EMD algorithm and approximate an appropriate MFP. This was studied in more detail by examining the MFP sensitivity to variations in acquisition window time and atomic velocity initial conditions.

2.1.2.6 LVDOS Sampling Window Size

LVDOS-EMD requires that simulations of all structures demonstrate that calculated LVDOS magnitude varies linearly as a function of FFT window size. A linear correspondence indicates that the underlying wavelet density is not changing over the measurement window. Any change in wavelet density relative to neighbouring segments over the measurement window will cause error in the approximation as a constant underlying structure with static
wavelet densities over the period of measurement is a requirement of the methodology. The velocity autocorrelation method does not provide an instantaneous measurement of phonon density. Longer time window periods are desired to reduce FFT windowing effects and improve spatial resolution. A consequence of using longer periods is that wavelets travel throughout the nanostructure during the sampling period, potentially causing blurring and double counting between adjacent segments. To verify that the LVDOS is reasonably unchanged over the 25 ps FFT windows size, the coefficient of determination was calculated for each frequency band \[ R_s(\omega)^2 = 1 - \frac{\sum_w (D_{s,w}(\omega) - f_{s,w}(\omega))^2}{\sum_w (D_{s,w}(\omega) - \overline{D}_s(\omega))^2}, \] where \( w \) represents the time window width (varied from 1-25 ps) used for all calculations, \( f \) is the regression linear fit, and \( \overline{D}_s(\omega) \) is the mean average of the LVDOS across all windows. Figure 2.12 shows high linearity of LVDOS calculations over a large time window size in regions of high occupation. This correlation indicates that despite high phonon velocity, regions of high and low density persist for the majority of the chosen time window. The coefficient of determination is smaller in bordering frequency bands with lower overall occupation as survivability and density are both small enough to prevent the formation of temporary, localized scattering regions. Similarly, thinner diameter nanowires exhibit poorer performance for this same reason. The high correlation in linearity of LVDOS of notched and unnotched nanowires, as evidenced in Figure 2.12, are consistent with the expectation of the Monte Carlo simulation shown in Figure 2.8, and its corresponding survivability equation, for both pristine and nanostructured simulations.

The proposed methodology works well in equilibrium scenarios where regions of collisions do not change in time, and the LVDOS does not vary significantly throughout the window of observation. These conditions should apply in the majority of solid, nanostructured materials. Satisfactory data sets from MD modelling results can be identified by observing a linear increase in the standard deviation of the LVDOS as a function of time window size, and an MFP mean that converges with increasing time window size.

A comparison of the calculated MFP of a straight and notched 4.9 nm diameter silicon nanowire is shown in Figure 2.13. The greater variation between trials of the straight nanowire demonstrates the lower precision in estimating the mean free path of a material with negligible structural variation. The mean free path of the straight nanowire is significantly longer than that of the notched equivalent, and both have MFPs on the same
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Figure 2.12: Studies using the MD results of simulations based on 3.8 nm (top), 2.7 nm straight and notched (middle), and 1.6 nm (bottom) silicon nanowires. a) Average frequency-dependent LVDOS, and b) coefficient of determination showing how well the spatially-averaged LVDOS for each segment increases linearly with FFT time window size.
order as the thickness of the nanowire, which is expected due to boundary scattering on the surface of the nanowire. Multiple simulations of the same nanowire with different atom starting velocities also yielded similar results, showing that the MFP is not dependent on phonon initial conditions for identical simulation procedures.

This method is most effective when the structure presents regions of significant scattering into otherwise unoccupied bands. Large structures that present very little variation in scattering rates along the direction of measurement will typically have scattering underestimated as phonons move between already occupied bands. It is also important to ensure that segments are small enough to capture shifts in VDOS caused by wavelet generation or scattering, and that the structure is symmetric around the axis of measurement. Standing waves and direct phonon exchanges between bands are neglected in this estimation as the former do not contribute significantly to thermal transport within the model and the latter would require the identification and tracking of individual phonons which would greatly increase computational cost.

Figure 2.13: Comparison of MFP calculation of a straight (top) and a roughened/notched (bottom) silicon nanowire 4.9 nm diameter. The roughened nanowire has 1.6 nm deep, 0.54 nm diameter notches every 5.4 nm along the length of the nanowire. The straight nanowire is shown as a mean average (black line) of four simulations with different starting conditions (grey overlay).
The computational simplicity of this method drastically reduces both computation time and memory requirements. Only $10^4$ simulation steps are necessary to calculate the VAF to sufficient resolution for LVDOS-EMD, and it can be calculated for each slice independently, allowing very large structures to be separated during simulation and formed into segments before a mean free path calculation takes place. This removes the need to store all atom velocities and positions in memory concurrently, further reducing computation requirements for analyzing large structures.

### 2.1.3 Methodology and Performance on Silicon Nanostructures

Results using LVDOS are compared with full MD results before (LVDOS-EMD) and after (LVDOS-NEMD) Mueller-Plathe simulation results for a variety of silicon nanostructured wires. LVDOS-EMD uses atom velocity ($z$-axis, or $\langle 001 \rangle$, only) and position data ($z$-axis, or $\langle 001 \rangle$, only) collected after completion of the aforementioned Mueller-Plathe simulation. LVDOS-EMD data is collected after relaxation over 25,000 iterations of velocity and position data acquisition. The highest occupied vibrational states are below 20 THz, allowing position and velocity data exports at 20 fs intervals without significant aliasing effects. A comparison of the LVDOS of each technique for both thin and thick nanowires is shown in Figure 2.14. The greater phonon density is visible in the thicker nanowire, resulting in a smoother LVDOS along the length of the nanowire and corresponding increase in mean free path. Results from EMD and NEMD data sets are shown to emphasize that they are similar, meaning that the LVDOS-EMD method can be expected to yield similar results with and without a temperature gradient.

The nanowires were simulated at a time step of 1 fs and a length of 217 nm (400 unit cells) to ensure that all phonon frequencies and wavelengths relevant to thermal conductivity were included. The chosen time step is similar to that used by others, although a slightly longer step size was chosen to reduce computational requirements with the understanding that direct comparisons to experimental results cannot be made. To further save memory and reduce computation time, a full length, 4.9 nm diameter nanowire was simulated, segmented, and analysed to determine the minimum necessary export structure size and running time.

A straight, 217 nm nanowire was simulated with the velocity data of all atoms exported. The simulation data was truncated in post-processing to determine that a running time of 25 ps and an 81 nm segment of the structure would be sufficient for the LVDOS analysis. The impact of nanowire length
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Figure 2.14: LVDOS profile for $k = 4.9 \text{ nm}$ (a,b) and $k = 1.6 \text{ nm}$ (c,d) silicon nanowires generated from EMD (a,b) or NEMD (c,d) simulations.

and simulation time on the LVDOS-EMD technique is shown in Figure 2.15. Export segment lengths of 80 nm and a running time of 25 ps were selected for these simulations. The variation in conductivity as a function of structure length is due to the minimum structural length required to ensure that the MFP is fully computed. Simulations of shorter, periodic structures can also be used, but the LVDOS-EMD algorithm must continue to operate through periodic boundary conditions to ensure that longer duration phonons are represented within the calculation.

Figure 2.16 shows the normalized thermal conductance of nanowires in various configurations using four different computational methods. The Mueller-Plathe method involved first relaxing the structure for 75,000 iterations, followed by 1,000,000 iterations of developing the thermal gradient along the structure, and 200,000 iterations to collect spatial temperature information under equilibrium conditions. The internal Mueller-Plathe
Figure 2.15: Thermal conductance using LVDOS-EMD as a function of exported silicon nanowire a) length data and b) time data based on 4.9 nm nanowires. Time data is normalized by calculated thermal conductance at 1 ps for each nanowire.
2.1. LVDOS-EMD

LAMMPS module was used with a swap configured every 500 simulation steps and the nanowire sliced into 20 segments\cite{121,140}. An example script is shown in Appendix F.

While developing the gradient, a weak Berendsen thermostat was used to maintain an average temperature near 300 K \cite{141}. Velocity data from atoms in a 80 nm long segment over a 25 ps span was collected after equilibration (LVDOS-EMD) and at the end of the simulation (LVDOS-NEMD). A single, straight silicon structure was sliced equally into segments 0.1 nm to 10 nm thick to determine the optimum slicing thickness, 0.135 nm, that yielded the least deviation in number of atoms per slice, assuming a minimum of 50 atoms/slice, over the entire structure. The same slicing thickness was then used for all structures. The VAF for each atom was calculated and summed for all the atoms in each segment (slice) to determine the LVDOS along the nanostructure. Finally, the MFP and thermal conductivity were calculated as described in Section 2.1.1. Of the four methods shown, the direct Mueller-Plathe method is considered to be the most accurate NEMD-based method for silicon\cite{107}.

Computations were also performed using $v_\beta(\omega)$ with results within 1% of computations performed using a frequency-invariant group velocity. Results assuming that vibrations only travel in one direction were also computed, using (2.16)-(2.17) instead of (2.25)-(2.28) to calculate MFP, yielding values within 1% of one another. The more comprehensive, bidirectional set of equations acts as a rolling average of the survival calculation. For simpler structures where the width of the segment is significantly smaller than any nanostructural features, equations (2.16)-(2.17) act as a reasonable approximation.

Molecular dynamics methods are particularly useful when studying structures with nanoscale features. To illustrate the utility of LVDOS-EMD over a modified bulk heat transfer model, Comsol Multiphysics®, a finite element analysis (FEA) solver, was used. Equivalent, ideal structures of notched silicon nanowires were constructed within Comsol where Mueller-Plathe MD simulation results for straight nanowires were used to provide the thermal conductivity of nanowire segments of various cross-sectional areas. An example of one such model is shown in Figure 2.17. Boundary conditions of 300 K and 400 K were set at opposite ends of the nanowire, and thermal flux was measured near the centre of the nanowire to calculate thermal conductivity.

Normalized FEA thermal conductance shows large errors compared to the MD-based techniques for thin, notched nanowires (Figure 2.16b/d). The error is likely due to enhanced phonon boundary scattering caused by the
2.1. LVDOS-EMD

Figure 2.16: Normalized thermal conductance of silicon nanowires by a) variable nanowire thickness of smooth nanowires, b) variable notch depth for \( k = 4.89 \text{ nm}, p = 5.43 \text{ nm}, w = 0.543 \text{ nm}, \) c) variable notch period for \( k = 2.72 \text{ nm}, D = 0.543 \text{ nm}, w = 0.543 \text{ nm}, \) and d) variable notch width for \( k = 3.80 \text{ nm}, D = 0.543 \text{ nm}, p = 5.43 \text{ nm}. \) Calculated thermal conductance is normalized to a) a 3.26 nm thick straight nanowire, b-d) an unnotched nanowire of similar thickness. The error bars show the variation in Mueller-Plathe simulation results for thermal conductivity.

morphology of the nanowire, which would not be considered within a bulk continuum simulation, even if it is provided information on thermal conductivity as a function of material cross-sectional area [92]. The enhanced scattering further reduces mean free path and the corresponding material thermal conductivities, although this behaviour can only be observed in atomistic scale models that incorporate the wave properties of phonons. LVDOS-EMD does capture some of these behavioural features, providing a more accurate calculation for thermal conductance. Errors could also be the result of variations in nanowire structure after molecular relaxation when compared to the ideal shape programmed within Comsol.

LVDOS-EMD and LVDOS-NEMD show similar normalized thermal con-
2.1. LVDOS-EMD

Figure 2.17: Comsol model of a notched nanowire where each segment is designated a thermal conductivity from Mueller-Plathe results of straight nanowires of identical thickness.

Conductance results, with small variations due to changes in mean free path and density of states resulting from the NEMD temperature gradient. The NEMD method also involves a much longer running time, allowing phonons additional time to stabilize. Compared to the FEA method, the LVDOS-EMD and LVDOS-NEMD methods more closely capture changes in thermal conductance resulting from phonon boundary scattering and reduced MFP, however both methods still deviate from Mueller-Plathe results as the nanowires increase in diameter. This deviation is likely due to a change in group velocity as the nanowires begin to develop bulk conductance properties.

The mean absolute error between the LVDOS-EMD method and Mueller-Plathe results is 12%, with the error of the unnotched nanowires contributing more significantly. To minimize this error, a reference nanowire with dimensions similar to the configurations under consideration should be selected. The time required to calculate all configurations using Mueller-Plathe, including the relaxation of the structure was 845 cpu days. The time required for the LVDOS-EMD method was 50 cpu days, for a reduction in simulation time of 17 fold. Eighty percent of the running time of the LVDOS-EMD simulations was structural relaxation, meaning that further improvements in algorithm performance are possible. Neglecting relaxation, LVDOS-EMD requires $40\times$ fewer simulation steps per structure.
2.1.4 Discussion of Validation

The LVDOS-EMD method proposed and demonstrated herein shows promise as a rapid computational methodology for exploring variations in thermal conductivity in similar structures, but there are significant limitations guiding the potential applications of the methodology. Only nanoscale materials with surface/structure phonon scattering as the dominant scattering mechanism and with small variations in structure at identical temperatures can be rapidly investigated. The calculation of wavelet mean free path is an approximation and thus more rigorous EMD and NEMD methods must be used to confirm observed material behaviours. Structures with complex configurations internal to the nanowire, or features that reduce the number of atoms per segment to less than 50, may also reduce the accuracy of the methodology.

Despite these shortcomings, LVDOS-EMD presents several opportunities. By studying the thermal conductivity of a material through its mean free path and LVDOS, phononic wave effects which might be ignored by continuum or FEA models can be included. LVDOS-EMD enables a predominantly qualitative comparative study of thermal conductance effects of small structural changes with MD simulations in less than 6% the duration of other NEMD and EMD methods when including molecular relaxation, and less than 0.1% if relaxation is not included. It can also function on very large structures by performing calculations on independent subsections prior to final post-processing, thereby reducing memory requirements. Although the assumption of consistent group velocity between simulations does limit the potential accuracy of the method, the dynamical matrix of the system need not be solved. If group velocity information is generated as part of the simulation then the information can be included in the calculations to produce more accurate results for varied structures. Further work on more complex structures must be done to determine the accuracy of the methodology over a wide range of temperatures, material systems, and structural configurations.

2.2 Zinc Oxide Nanostructures

ZnO as a material system has very different properties than silicon, and it is therefore necessary to run simulations using the ZnO material system to explore Al:ZnO nanostructures with amenable thermoelectric properties. The basic structure of ZnO used for these molecular dynamics simulations was nanowires as shown in Figure 2.18. For bulk simulations, a fully periodic
supercell either $5 \times 5$ unit cells in size or $8 \times 8$ unit cells in size was used.

Figure 2.18: The $5 \times 5$ unit cell ($5$ unit cells along the long, outside edge) ZnO nanowire configuration used for MD simulations is shown. Red atoms are zinc and grey atoms are oxygen. The image is rendered using VMD\cite{49}.

The overarching motivation of simulating ZnO nanostructures was to examine the comparative thermal properties of various nanostructures and assess their relative thermoelectric performance. Computational limitations necessitated performing simulations on structures that could not be experimentally synthesized due to their small size or poor stability. This section presents an analytical framework that can be applied to larger structures to derive more meaningful, quantifiable results to better guide thermoelectric research, but, as presented, certain limitations in the modelling approach must be elucidated.

- The heavily ionic composition of ZnO places additional computational constraints on modelling the material as discussed in Section 2.2.1. The corresponding additional computational requirements further limit the length and width modelled structures when compared to silicon. Structures presented in this section typically required 7 days to compute data sets suitable for Mueller-Plathe using 128 CPU cores.

- The small size of the nanostructures herein examined can provide some insight into larger, bulk materials. Extrapolating small structures into bulk materials using the Matthiessen Law is discussed in Section 2.2.2.
Table 2.1: MD NEMD results for simulations of $8 \times 8 \times 200$ unit cell, fully periodic ZnO bulk simulations showing relaxation lattice constants and calculated thermal conductivity for three different force field models.

<table>
<thead>
<tr>
<th>Force Field</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\kappa$ (W m$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wolf</td>
<td>3.18</td>
<td>5.02</td>
<td>29.4</td>
</tr>
<tr>
<td>Pedone</td>
<td>3.08</td>
<td>5.27</td>
<td>34.1</td>
</tr>
<tr>
<td>ReaxFF</td>
<td>3.29</td>
<td>5.32</td>
<td>15.0</td>
</tr>
<tr>
<td>Experimental$^{[47]}$</td>
<td>3.25</td>
<td>5.21</td>
<td>$37 - 147$</td>
</tr>
<tr>
<td>Ab Initio$^{[144]}$</td>
<td>N/A</td>
<td>N/A</td>
<td>62</td>
</tr>
</tbody>
</table>

Extrapolation assumes that the structure is possible to synthesize as a bulk material without changing feature size, which is not a reasonable assumption for the proposed electrochemical method. Therefore, although MD results were used to inform experimental work, a direct comparison between modelled and experimentally grown structures cannot be drawn.

- A proper examination of the improvement of the thermoelectric properties of a material due to nanostructuring requires considering the impact of structures on thermal and electronic material parameters. Electronic modelling of ZnO is also computationally intensive due to the involvement of core electrons in Zn-O bonding behaviour. Classical consideration of electronic behaviour is discussed in Section 2.2.3, but neglecting quantum effects adds substantial error to structures with features on the order of angstroms.

### 2.2.1 Molecular Dynamics Simulation of ZnO

Multiple force field models were considered and tested for their accuracy and speed in simulating the thermal and structural properties of ZnO. The choice of force field was constrained by the strongly ionic and binary nature of the crystal. The force field had to provide accurate modelling of phonon propagation for thermal conductivity calculations, accommodate interactions with other elements, and support molecular rearranging such as those resulting from thermal annealing. Three ZnO force field models, Wolf$^{[129]}$, Pedone$^{[128]}$, and ReaxFF$^{[109, 130, 142, 143]}$ were examined. The lattice constants and bulk thermal conductivity calculated by relaxing identical ZnO nanowires until thermal equilibrium using the corresponding force field, followed by a NEMD measurement are summarized in Table 2.1.
2.2. Zinc Oxide Nanostructures

Although Wolf and Pedone force fields both operated up to 5× faster than ReaxFF, ReaxFF produced lattice constants closer to the experimental values of ZnO and also afforded the ability to examine changes in chemical bonding between systems of mixed material systems such as heterostructures. For these reasons, and the demonstrated accuracy of ReaxFF in thermal conductivity calculations of ZnO, ReaxFF was selected[130]. ReaxFF is a model based on \textit{ab initio} calculations of potentials and charges between two atoms, and includes off-diagonal terms, torsions, angles, and forces between all combinations of atom and bonds. The set of coefficients selected included interactions between zinc, oxygen, and hydrogen. The hydrogen coefficients were not generally used for the simulations performed herein, but were used for special cases where the behaviours of zinc and ZnO in water were explored.

There is a significant error between bulk thermal conductivity of simulated ZnO and experimental ZnO in Table 2.1. Simulating the bulk using Mueller-Plathe can be constrained by the inability of the system to accommodate the wavelengths and full mean free path of the phonons[101, 145]. A method to derive the thermal conductivity despite this limitation is to simulate the same structure under identical conditions at different lengths and then plot the inverse thermal conductivity against the inverse structure length. The resulting plot should be linear and the y-axis intercept can be used to extrapolate the thermal conductivity of a simulated structure of infinite length[101]. Figure 2.19 shows the results of this test using ReaxFF on ZnO which provides a thermal conductivity of $55 \pm 15 \text{ W m}^{-1}\text{K}^{-1}$, comparing favourably with other modelled thermal conductivity estimations of $62 \text{ W m}^{-1}\text{K}^{-1}$[144].

The simulation was performed with a $8 \times 8 \times 300$ unit cell parallelogram prism nanowire of ZnO oriented along $(002)$ with triclinic, periodic boundary conditions using a $0.5\text{ fs}$ time step, $500,000$ NPT relaxation steps, and $2,600,000$ Mueller-Plathe steps using NVE conditions. The large degree of scattering around the linear fit in the plot is likely due to inconsistent additional contributions to thermal conductivity by new phonons of longer wavelength. The MFP of phonons in ZnO can also exceed the length of the simulation cell. Based on the thermal conductivity calculations at shorter lengths, a simulation over $1 \mu\text{m}$ in length would be necessary to properly calculate the thermal conductivity of bulk ZnO. Full simulation details can be found in Appendix F.3.

Although another method, such as Green-Kubo, could be used to calculate the thermal conductivity of the bulk material and nanostructures, Green-Kubo does not perform very well with structurally complex materials.
Figure 2.19: A plot of inverse, simulated, bulk ZnO thermal conductivity using Mueller-Plathe against inverse simulation cell length. The lengths simulated range from 50 unit cells (26 nm) to 300 unit cells (156 nm). Two thermal conductivities were calculated per length with the results being averaged. Uncertainty at each length is within 0.5 W m$^{-1}$ K.

and may not converge\cite{119, 120}. Green-Kubo is also typically performed on smaller supercells and would require significant computational resources to model nanostructured materials with long sections of aperiodic features due to the need to average multiple simulations\cite{107, 119}.

Simulation time steps of 0.25 fs, 0.5 fs, and 1.0 fs were tested on 5 × 5 × 200 unit cell nanowires using ReaxFF. There was not a significant difference in thermal conductivity results between simulations operating at 0.25 fs and 0.5 fs, however simulations operating at 1.0 fs yielded a thermal conductivity significantly higher, demonstrating poor suitability. As simulations using ReaxFF are very computationally intensive, a time step of 0.5 fs was chosen. Using NEMD to determine the thermal conductivity of a single 5 × 5 × 200 unit cell nanowire required 6 days and 50 GB of memory when using 128 cores.
2.2. Extrapolating from Nanostructures to Bulk

Due to the computational resources required to examine nanowires and nanostructures on size scales congruent with experimental work, a $5 \times 5 \times 200$ unit cell nanowire aligned along the $z$-axis was chosen for all nanostructural simulations. By using a nanowire with a highly constraining diameter, the MFP of phonons was necessarily less than the length of the simulated structure, allowing thermal conductivities to be calculated without the need to use multiple length steps and extrapolation. A consequence of this effect is that any thermal reduction resulting from the examined nanostructural features will be influenced by the surface scattering effects of the nanowire. A method to compensate for this effect involves the Matthiessen rule,

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{boundary}}} + \frac{1}{\tau_{\text{defects}}} + \frac{1}{\tau_{\text{feature}}} + \ldots, \quad (2.48)$$

where $\tau$ is the phonon lifetime, which is proportional to the mean free path. The Matthiessen rule indicates that the influence of each nanostructural feature on the overall MFP of the system can be expressed as an inverse summation of the individual mean free paths. While the surface effects of the nanowire will play a significant role in the reduction of thermal conductivity, assuming this effect is the same for each simulation, any further reduction in mean free path is attributable to the effects of additional nanostructuring imposed on the material. To leverage this consistency, identical starting nanowires are used in all simulations and no comparisons are made with bulk materials.

2.2.3 Electronic Modelling

Concurrently with phononic studies, electron transport studies were also performed to determine if examined structures maintained a high electrical conductivity and Seebeck coefficient. The Seebeck coefficient is predominantly a function of material bandgap and Fermi energy, meaning that structural changes, provided their effects remain classical in the electronic domain, should not have a significant effect [16]. In both classical and quantum models, electrical conductivity is strongly affected by changes in material structure.

Rigorous quantum calculation of electron transport was explored in detail with results discussed briefly in Appendix A.1. For pragmatic reasons owing to the simulation time required for quantum electronic simulation of ZnO, a classical approximation for modelling electronic behaviour in the
2.2. Zinc Oxide Nanostructures

examined nanostructures was selected. In this approach, the nanowire was segmented along the \( z \)-axis into thin slices of atoms. These slices were each superimposed on a dense grid of squares to determine the effective cross-sectional area defined by atoms within the slice. The slices were then assigned effective resistance based on their area and were summed in series to produce an effective resistance for the entire wire. This method allowed the accommodation of very large structures with high densities of localized, random defects dispersed throughout. Atoms were assigned point volumes and lines were drawn between originating atoms and 10 nearest neighbours to improve coverage on the area map. The number of nearest neighbours was selected to maximize the discernment between occupied and unoccupied regions in the structure. All area calculations were performed on structures after molecular dynamics simulations in order to incorporate any twisting, distortion, and other irregularities in the structures resulting from the structural modifications. An example of a slice examined for atomic occupation is shown in Figure 2.20.

![Cross-sectional slice of a hexagonal nanowire consisting of irregular voids showing the grid of squares used to determine occupation for area calculations. Points representing the atoms were first overlayed onto the grid squares and then lines were drawn between nearest and next nearest neighbours to fill in the space between atoms.](image)

Figure 2.20: Cross-sectional slice of a hexagonal nanowire consisting of irregular voids showing the grid of squares used to determine occupation for area calculations. Points representing the atoms were first overlayed onto the grid squares and then lines were drawn between nearest and next nearest neighbours to fill in the space between atoms.
2.2. Zinc Oxide Nanostructures

The nature of the approximation neglects quantum effects such as confinement, tunneling, and conduction limits imposed by the Pauli exclusion principle in very narrow segments of the nanowires. Given the scale of the structures under consideration, the classical model overestimates the conductivity of the structures considered herein. Although quantum tunneling may offset some of the conductivity losses due to confinement and electron band availability, its effect is comparatively small. Other effects such as reduced electronic mean free path in some structures will also further limit electron transport, where electronic MFP is $5 \text{Å} - 50 \text{Å}$ [146]. The classical model employed applies the same rules to all structures and uses normalized results based on a straight nanowire to better reflect the restricted predictive capabilities of this model.

2.2.4 Structural Thermoelectric Enhancement Factor

A new term, the Structural Thermoelectric Enhancement Factor (STEF), $\xi$, of the nanostructure is defined as

$$\xi = \frac{A}{K_{\text{lattice}}\xi_{\text{ref}}}.$$  

STEF is a performance metric representing the ratio of effective cross-sectional area (see Section 2.2.3) to thermal conductance for structures of identical length. The normalization term, $\xi_{\text{ref}}$, is determined using a reference material with no nanostructural modifications, a straight nanowire in this work. It is conceptually similar to comparing the thermal resistivity for structures of equal length, but differs in that it represents a material with a cross-sectional area that varies throughout its length rather than the periodic, uniform structure used for conventional thermal resistivity. When used to compare similar structures, it indicates how effectively modifications to the structure reduce thermal conductivity relative to the reduction in classical electronic conductivity.

2.2.5 Intrastructural LVDOS-EMD

One limitation of the LVDOS-EMD method as presented in Section 2.1 is that it assumes no structural variation along the $x$-$y$ plane of the nanostructure. This assumption is safe if the nanostructural features are predominantly on the outer edges of the nanowire, but in some structures where the features appear randomly throughout the bulk in high densities, such as in nanowires with random voids, characteristics of the phonon interaction
immediately around these structures may be lost. To accommodate for this effect, an intrastructural LVDOS-EMD method was developed that breaks apart each structure after simulation into extremely thin nanowires less than 1 nm × 1 nm in cross-sectional area that span the length of the original structure. LVDOS-EMD was employed on each thin nanowire, yielding multiple parallel thermal conductance calculations for each nanostructure. In order to maintain the minimum requisite number of atoms in each segment, the segment length along the z-axis had to be increased. Another restriction is that wavelets travelling in a diagonal direction are not as accurately represented; the assumption is made that wavelets travel nearly parallel to the z-axis. A fully 3D Monte Carlo method with random pathing throughout the structure was considered to improve accuracy, but the computational cost overcomes the benefit the LVDOS-EMD methodology.

A further enhancement to the original theory is to render the full structure periodic along the z-axis and vary the starting position for the MFP calculation along its entire length. If the nanostructural effects are not consistently periodic along the z-axis over short distances, calculating the MFP only once at the origin can trivialize structural features located further along the nanowire. By calculating a new MFP at several points along the wire and producing an MFP as a function of z-axis origin, structures with less periodicity were better represented.

By combining the two above enhancements, the intrastructural LVDOS-EMD methodology produced a matrix of thermal conductances with origins throughout the x, y, z volumetric space of the simulated nanowire. To yield a final thermal conductance, individual thermal conductances calculated with the same z-axis origin were summed. The resulting conductance, which is only a function of starting position along the z-axis, was then reduced to a final conductance using an inverse sum. The performance and limitations of this methodology are explored in the following sections.

2.2.6 Straight Nanowires

A straight, hexagonal ZnO nanowire was simulated to act as a reference for other structures studied in this section. The longer edge of the nanowire in the x-y plane is 16.05 Å long, and the nanowire is 1060 Å long along the z-axis prior to relaxation. The cross-sectional area of the nanowire prior to simulation is 6.73 × 10^{−18} m^2. A segment of the nanowire can be seen in Figure 2.18. The simulations were performed using the LAMMPS MD simulation engine over approximately three million iterations at a time step of 0.5 fs. NPT/NVE equilibration took place over 200,000 iterations.
with the Mueller-Plathe swapping process occurring over 2,600,000 iterations. Detailed scripts showing all simulation parameters can be found in Appendix F.

Length-wise cutaways through the centres of the nanowires are shown in Figure 2.21. The relaxation of the straight nanowire involved small variations in the total length of the simulation box, resulting in a slight deformation of the nanowire along the z-axis. A periodic boundary condition is assumed along the z-axis and no stress was applied to the wire. The Mueller-Plathe methodology was discussed in Section 2.1. The thermal conductivity of the straight nanowire resulting from the reverse NEMD simulations was $4.4 \pm 0.4 \text{W m}^{-1} \text{K}^{-1}$, representing a $12.5\times$ reduction in lattice thermal conductivity compared to the simulated bulk material. The LVDOS plot, shown in Figure 2.22, shows three major optical phonon bands and one major acoustic phonon band. The optical and acoustic phonon bands are well separated and contained few variations in phonon DOS along the length of the wire, which indicates that, with the exception of surface scattering effects, there are no major nanostructural influences on phonon propagation. The effective cross-sectional area after relaxation calculated by summing the measured area of all slices, as discussed in Section 2.2.3, is $501 \text{\AA}^2$. 

2.2. Zinc Oxide Nanostructures
Figure 2.21: The cross-section of a variety of ZnO nanostructured materials post simulation. Red dots are zinc atoms and blue dots are oxygen atoms.
2.2. Zinc Oxide Nanostructures

2.2.7 Hollow Nanowires

Hollow nanowires or nanotubes are shaped as an extruded ring of ZnO. By reducing the size of the material as with straight nanowires, a reduction in lattice thermal conductivity can be realized. This reduction is due to anharmonic scattering of phonons against the surfaces of the nanowire. By removing the core of the nanowire, the scattering mechanism can be enhanced by offering another boundary against which to scatter. A cutaway of a hollow nanowire is shown in Figure [2.21]. Removing the core of the nanowire reduces its structural strength and affects the lattice constants throughout the material by adding dangling bonds at the new surface. The LVDOS of phonons within the hollow wire, shown in Figure [2.23], indicates lower band availability for phonon occupation due, in part, to the reduced cross-sectional area of the nanowire. The brighter bands that were particularly visible in the LVDOS of the straight nanowire have also disappeared indicating that harmonic bands are less clearly defined. This reduced definition is likely the result of greater variation in lattice spacing.

Figure 2.22: An image showing the LVDOS of a straight, 104 nm long, 5 × 5 unit cell, hexagonal ZnO nanowire oriented along the z-axis.
Figure 2.23: An image showing the LVDOS of a hollow, 104 nm long, 5 × 5 unit cell, hexagonal ZnO nanowire oriented along the z-axis.

The performance of the structure can be seen in Figure 2.24. As the radius of the etch through the centre of the nanowire increases, the effective area for electron transport through the nanowire decreases. Etching the nanowire beyond a radius of 5 Å caused the nanowire to collapse during simulation. Despite this limitation, it is clear from the data collected that hollow nanowires do have a lower thermal conductivity than filled nanowires, however the reduction in cross-sectional area for electron transport within the bulk of the nanowire offsets any gains caused by reduced phonon transport.

Large, hollow nanowires with walls nanometres in thickness are successfully fabricated at much larger diameters using a variety of single and multistep processes, including electrodeposition [40]. The thermal properties of hollow ZnO nanowires have not been experimentally measured and compared to their bulk equivalents. Although it may be possible to fabricate hollow nanowires as modeled herein, such structures have not yet been experimentally synthesized.
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Figure 2.24: A plot showing the effective area, simulated thermal conductivity, and normalized STEF of hollow nanowires as a function of etching radius.

2.2.8 Heterostructured Nanowires

Heterostructured materials are composite materials consisting of thin, alternating layers of different materials. The heterostructure considered in this application is a superlattice consisting of alternating zinc and ZnO layers. If the deposition process is starved of oxygen by increasing the applied voltage during electrodeposition, then metallic zinc may be deposited, allowing for the formation of a zinc/ZnO heterostructured material. Heterostructures simulated consisted of 2-10 unit cells of each material stacked throughout. Heterostructures with such frequent oscillations between materials are possible to fabricate using vacuum deposition techniques but have not been demonstrated repeatably using electrochemistry. They are considered to be excellent candidates for thermoelectric materials as each transition between material systems forms a boundary layer which can interfere with phonon transport. Electronically, using materials of different bandgaps can also allow for band tailoring, such as creating regular barriers within the structure to assist with electron energy confinement or blocking the transport of lower energy electrons and improving entropic reversibility using energy-filtering[50]. Heterostructures are difficult to fabricate as the deposition process must cleanly and rapidly cycle between materials. They also
tend to demonstrate poor mechanical properties due to lattice mismatches at each boundary. In the case of zinc and ZnO, the former is a hexagonal closely packed lattice and the latter is wurtzite, which are not well matched in lattice shape. The resulting superlattice nanowire is shown in Figure 2.21.

The LVDOS of a superlattice with 8 unit cells of ZnO and 8 unit cells of Zn can be seen in Figure 2.25. The division between materials is very apparent. The ZnO band contains both significant quantities of optical and acoustic phonons, whereas the zinc metal LVDOS is composed only of acoustic phonons as zinc metal is monatomic. On closer examination of the optical bands at the interface, significant crossband scattering is apparent by the very low density of optical phonons in Zn segments of the heterostructure. The asymmetry of the scattering is caused by ZnO presenting wurtzite zinc on the left and wurtzite oxygen on the right of the hexagonal zinc lattice. The acoustic band also shows significant differences in occupation between zinc and zinc oxide, creating boundaries in the material interfaces that promote phonon collision. These regular, enhanced scattering regions at material interfaces greatly reduce thermal conductivity.

Figure 2.25: An image showing the LVDOS of a superlattice, 104 nm long, 5 × 5 unit cell, hexagonal ZnO nanowire oriented along the z-axis.
2.2. Zinc Oxide Nanostructures

Table 2.2: Results of ZnO heterostructure simulations showing effective area, simulated thermal conductivity, and the normalized effect of changing the periodicity of Zn-ZnO superlattice nanowires for superlattice configurations involving different sizes of zinc and zinc oxide segments.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Effective Area (Å²)</th>
<th>Thermal Conductivity (W m⁻¹ K⁻¹)</th>
<th>STEF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heterostructures</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn (8 uc) / ZnO (8 uc)</td>
<td>500</td>
<td>1.87</td>
<td>2.35</td>
</tr>
<tr>
<td>Zn (4 uc) / ZnO (6 uc)</td>
<td>499</td>
<td>1.1</td>
<td>3.98</td>
</tr>
<tr>
<td>Zn (6 uc) / ZnO (4 uc)</td>
<td>500</td>
<td>1.13</td>
<td>3.89</td>
</tr>
<tr>
<td>Zn (4 uc) / ZnO (4 uc)</td>
<td>501</td>
<td>1.04</td>
<td>4.23</td>
</tr>
</tbody>
</table>

The results from thermal conductivity simulations are shown in Table 2.2. Favouring one material over the other in the overall composition of the nanowire had little effect, however the number of boundaries created did play a prominent role in reducing the thermal conductivity of the nanowire. One major limitation of fabricating a superlattice nanowire using zinc is that the low melting point of zinc metal would limit the operation of the thermoelectric module to under 400°C, which is a prohibitive limitation for a module that would otherwise achieve peak conversion efficiency near 1000°C. Other metals with higher melting temperatures or semiconducting oxides such as aluminum oxide should be considered to complement ZnO in a superlattice configuration. Electron transport across the boundaries would also be impinged, which is not considered within the electronic transport method used herein. As a result, the thermoelectric performance of the material is likely to be poorer than what is shown in the table.

2.2.9 Nanovoided Nanostructures

Nanovoids are small, vacant shapes such as spheres within either lower dimension or bulk material. The voids serve as defects or scattering boundaries for phonon travel. Voids in a straight, simulated nanowire were produced by first defining a rectangular prism around the nanowire then randomly selecting (x,y,z) coordinates within the prism. The radius of each spherical void was determined by multiplying a given mean radius by a randomly selected scaling factor between 0.5 and 1.5. Voids were generated until the total volume of spherical voids exceeded the specified ratio of void space to nanowire space. The simulation were carefully studied, with randomization...
2.2. Zinc Oxide Nanostructures

seeds varied to generate structures capable of maintaining integrity until the desired void density was achieved. Void density was constrained by the stability of the nanowire structures. A cutaway of a nanovoided nanowire is shown in Figure 2.21.

Using LVDOS to examine the phonon behaviour around voids is more difficult as the nanowire is asymmetric on every axis. An LVDOS plot that uses conventional LVDOS described in Section 2.1 is shown in Figure 2.26. The LVDOS is chaotic with many gaps and noisy bands indicative of significant phonon scattering and lattice interruptions. Regions of particularly high void density cause small gaps in the LVDOS as phonon occupation diminishes significantly. Additional scattering to the region between optical and acoustic phonons is also visible, further illustrating the effect of lattice defects on the LVDOS.

![Figure 2.26](image)

Figure 2.26: An image showing the LVDOS of a randomly voided nanostructure with spherical voids 3.0 ± 1.5 Å in size and representing 20% of the total volume of the 104 nm long, 5 × 5 unit cell, hexagonal ZnO nanowire oriented along the z-axis.

Thermal conductivity was calculated using NEMD for a series of ZnO nanowires with a specific set of random voids at varying densities. The
2.2. Zinc Oxide Nanostructures

LVDOs-EMD plots were also prepared for the same set of nanowires by progressively introducing voids to a nanowire within the LAMMPS environment. Only one simulation was required to produce LVDOs-EMD results for 14 different void configurations as additional voids could regularly be added throughout the simulation followed by settling periods and data collection. The results were then passed through conventional LVDOs-EMD which calculated thermal conductivity at one position in the nanowire and sliced the nanowire along the \( x-y \) plane. Intrastructural LVDOs-EMD was also employed by expanding the length of the segments along the \( z \)-axis and constraining \( x-y \) axis segment size to 1 nm \( \times \) 1 nm. The length along the \( z \)-axis had to be increased to ensure that a statistically significant number of atoms (>50) remained within each segment. 20 sets of thin nanowires and their \( z \)-axis thermal conductances were generated prior to combining all the elements into a single thermal conductance as described in Section 2.2.5. If a void was encountered that completely severed the thin nanowire, the MFP was necessarily truncated, leading to a much lower thermal conductivity. In cases where the nanowire randomly started within a void, a thermal conductivity of 0 was used. Since segments of all thin nanowires representing the same position along the complete nanowire were first averaged, nanowire thermal conductivity could be calculated for a variety of void configurations up to 50% volumetric void density. The results are shown in Figure 2.27.

Increasing the number of voids in the material consistently improved the thermal conductivity and \( \xi \) until voids had consumed approximately 30% of the original volume of the material. Although LVDOs-EMD results showed the same trend, the magnitude of the impact of the voids on the thermal conductivity of the material was less. In the case of simple LVDOs-EMD, the random dispersion of voids within the slices tended to average the LVDOs of each slice, underestimating the impact of the voids on the mean free path. Although the intrastructural LVDOs-EMD did compensate more successfully for this effect, lengthening the slices along the \( z \)-axis yielded a similar problem where multiple voids would fit into the same slice, inaccurately representing void configuration and their effect on the thermal conductance.

To confirm this effect, a second set of simulations were run for larger radius voids, shown in Figure 2.28. In these results, both the simple and intrastructural methods produced relative thermal conductivities much closer to the value expect from the NEMD calculation. Simulations with larger diameter voids resulted in unstable structures at void volumetric densities above 40%.

The overall performance of voided nanostructures is high, with STEF
scores above 5 as shown in Figure 2.29. Nanowires simulated with different random seeds showed similar promise. It should be noted that the high density and proximity of voids would likely interfere with electron propagation through the material, detrimentally impacting electrical conductivity in a fabricated device. The benefits of a voided structure have also been demonstrated through simulations and in nanobulk and similar experimentally-realized materials[30, 31, 62, 69, 149–152]. Some have also built analytical models in an attempt to describe the best void configuration for a given material, although these models are generally purely classical and neglect phonon wavelike behaviour[149].

2.2.10 HCP-Voided Nanostructures

A hexagonal close packed (HCP) structure is one that maximizes the number of spheres within a given volume. An analogy to an HCP lattice is that the atoms are positioned as though they are stacked bowling balls or cannon sockets.
2.2. Zinc Oxide Nanostructures

Figure 2.28: A chart plotting the NEMD, simple LVDOS-EMD, and advanced (intrastructural) LVDOS-EMD thermal conductivities as a function of void density for ZnO nanowires. The voids are 5.0 ± 2.5 Å in radius and 525 voids represents 40% of the volume of the nanowire.

balls. An HCP voided lattice is one that takes advantage of the benefits of voids within a structure, but rather than applying the voids randomly, the voids are integrated into the material in an HCP configuration, maximizing void density while preventing any overlap. Structures tested with maximum void density such that the edges of voids touched one another within the lattice yielded a structure that collapsed or lost atoms during the simulation. To improve nanostructure stability, the space between voids was increased by reducing their radius while holding their positions constant. A cut away of an HCP lattice is shown in Figure [2.21] and the LVDOS plot can be seen in Figure [2.30].

HCP voided structures were tested with void radii of 3 ± 1 Å. Despite consuming more volume in the nanostructure, the reduction in thermal conductivity was not as significant as with random voids, with 1.0 W m⁻¹ K⁻¹ being the lowest achieved thermal conductivity in any HCP configuration. The corresponding $\xi = 3.8$ at its best, indicating that although integrating the voids still improved the performance of the material, fully random voids
2.3. Comparison and Summary of ZnO Nanostructures

2.3.1 Comparison of Modelling Results

A summary of many simulations performed can be found in Table 2.3. Reducing the dimensionality of ZnO from a bulk material to a small diameter nanowire demonstrated a 12.5× drop in thermal conductivity relative to the bulk material, predominantly due to enhanced surface scattering at the surface of the nanowire. This behaviour is expected with the increase in surface area to volume ratio. Of the structures examined, heterostructures and randomly voided structures demonstrated the greatest reduction in thermal conductivity to cross-sectional area. In simulation, the heterostructures performed best when layer transitions occurred very frequently, such as every four unit cells of material (approximately 2 nm), although transitions that rapid cannot be realized through electrochemical deposition. Voided nanostructures functioned best with very small diameter voids (<1 nm) at densities of nearly 30% the volume of the material. Similarly, such a voided

Figure 2.29: A plot showing the effective area, simulated thermal conductivity, and normalized STEF of voided nanowires as a function of void density for $R = 3.0 \pm 1.5$ Å voids.

produced greater benefits for thermoelectric materials.
2.3. Comparison and Summary of ZnO Nanostructures

Figure 2.30: An image showing the LVDOS of a 104 nm long, 5 × 5 unit cell, hexagonal ZnO nanowire with 3 Å radius spheres removed in hexagonal closely packed configuration with sphere centers 10 Å apart.

material cannot be fabricated using known electrochemical methods, but structures with larger voids will be investigated.

The thermal properties of Al:ZnO are assumed to behave similarly to ZnO for the same structural modifications. Doping ZnO with aluminum consistently reduces the thermal conductivity of the material by a 2-6× factor by adding defects into the material and thereby creating additional scattering sites for phonons.[32, 52, 53, 62, 153]. Some adjustments to the ZnO models would be necessary for determining optimized nanostructural features such as nanovoid size for the Al:ZnO material system.

By using (2.48), results for modelled structures based on nanowires can be roughly extrapolated to a bulk material by removing the nanowire boundary contribution to reducing mean free path. At best, exclusively heterostructured bulk Al:ZnO and exclusively nanovoided bulk Al:ZnO would provide thermal conductivities of 1.32 W m⁻¹ K⁻¹ and 0.77 W m⁻¹ K⁻¹, respectively. The heterostructured configuration is anticipated to have a higher electrical conductivity than a pure Al:ZnO bulk material due to the
2.3. Comparison and Summary of ZnO Nanostructures

Table 2.3: Summary of the area calculations used to estimate classical electronic conductivity, thermal reverse NEMD conductivity calculations, and STEF for each modelled nanostructure.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Adjusted Area (Å²)</th>
<th>Thermal Conductivity (W m⁻¹ K⁻¹)</th>
<th>STEF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Straight</td>
<td>501</td>
<td>4.4</td>
<td>1</td>
</tr>
<tr>
<td>Voided Structures</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R = 3.0 ± 1.5 Å, 30% density</td>
<td>397</td>
<td>0.66</td>
<td>5.3</td>
</tr>
<tr>
<td>R = 3.0 ± 1.5 Å, 50% density</td>
<td>355</td>
<td>0.76</td>
<td>4.1</td>
</tr>
<tr>
<td>R = 5.0 ± 2.5 Å, 40% density</td>
<td>352</td>
<td>1.3</td>
<td>2.4</td>
</tr>
<tr>
<td>Hollow Structures</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R = 2 Å</td>
<td>460</td>
<td>2.9</td>
<td>1.4</td>
</tr>
<tr>
<td>R = 3 Å</td>
<td>423</td>
<td>3.2</td>
<td>1.2</td>
</tr>
<tr>
<td>R = 4 Å</td>
<td>346</td>
<td>1.5</td>
<td>2.0</td>
</tr>
<tr>
<td>R = 5 Å</td>
<td>283</td>
<td>1.9</td>
<td>1.3</td>
</tr>
<tr>
<td>Heterostructures</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn (8 uc) / ZnO (8 uc)</td>
<td>500</td>
<td>1.9</td>
<td>2.4</td>
</tr>
<tr>
<td>Zn (4 uc) / ZnO (6 uc)</td>
<td>499</td>
<td>1.1</td>
<td>4.0</td>
</tr>
<tr>
<td>Zn (6 uc) / ZnO (4 uc)</td>
<td>500</td>
<td>1.1</td>
<td>3.9</td>
</tr>
<tr>
<td>Zn (4 uc) / ZnO (4 uc)</td>
<td>501</td>
<td>1.0</td>
<td>4.2</td>
</tr>
<tr>
<td>HCP Voids</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R = 3 Å, spaced 8 Å</td>
<td>361</td>
<td>1.1</td>
<td>3.0</td>
</tr>
<tr>
<td>R = 3 Å, spaced 10 Å</td>
<td>433</td>
<td>1.0</td>
<td>3.8</td>
</tr>
</tbody>
</table>

integration of metal Zn layers, and the nanovoided material would lose 30% of its volume, with a corresponding 30% minimum drop in electrical conductivity. Practically, if the modelled void densities and sizes could be achieved, the electrical conductivity would drop more than the proposed 30% due to a reduction in electron mean free path. Full, quantum scale electronic modelling would be necessary to accurately determine electronic conductivity for the proposed nanovoided structures.

LVDOS-EMD was useful for studying the behaviour of phonons at interfaces within the nanostructures and provided some insights into the optimization of the materials. Figure 2.31 shows a summary of many structures simulated using simple LVDOS-EMD, advanced (intrastructural) LVDOS-EMD, and NEMD. There is good agreement in simpler, axisymmetric structures such as heterostructures, but there remains greater discrepancy in
structures presenting a large degree of asymmetry and randomness. All nanostructural effects were applied at exceptionally small scales, and one would expect better performance from LVDOS-EMD at larger scales where the features under consideration are larger than the slices used for studying the material.

Figure 2.31: A plot showing simple and advanced (intrastructural) LVDOS-EMD and NEMD results for a variety of structures. The intrastructural LVDOS-EMD results show the thermal conductivity determined for each thin segment as well as the average and standard distribution.

2.3.2 Summary of Modelling Results

Molecular dynamics modelling work began with the development of a rapid thermal conductivity prediction tool for nanostructures, called LVDOS-EMD. This tool was used to study the local density of states of phonons around nanostructural boundaries to determine the relative effect of these
2.3. Comparison and Summary of ZnO Nanostructures

boundaries on phonon propagation. The model, which worked well for the simple nanostructural features of a monatomic species like silicon, was enhanced to study ZnO with more complex structural properties such as nanovoids. Good agreement was found when comparing the intrastructural LVDOS-EMD method with NEMD results for ZnO, enabling the rapid prediction of changes in thermal conductivity of nanowires with varying void densities and radii. A voided structure, which is difficult to model, was also used to demonstrate the lower limitation of the statistical nature of LVDOS-EMD, where voids smaller than the slices used to study the material caused LVDOS-EMD to underestimate the effect of the feature. LVDOS-EMD is further constrained by the approximation method used for determining the wavelet mean free path and the requirement that the material structure be the dominant scattering mechanism in the material.

Reducing the thermal conductivity of a material by increasing its surface area to volume ratio is an established method, but one that has implications on electron transport as well. Calculating the electronic properties of the materials examined at the quantum scale was determined to be out of scope for this work, and a rough, classical approximation was used instead. The cross-sectional area of slices along the modelled nanostructures was calculated to produce an effective cross-sectional area for the material. This method would account for choke points along the material and other substantial variation in material dimensions, but neglected quantum and some size effects, limiting its accuracy at the nanometre scales considered. The thermal conductivity and effective cross-sectional area were combined to produce a performance metric, the STEF, to rate the relative benefit of the nanostructural modification.

A combination of LVDOS-EMD and conventional NEMD was used to analyze ZnO nanotubes, heterostructures, very low diameter nanowires, nanovoided nanowires, and HCP voided nanowires. By applying the Matthiessen rule, enhancements in performance due to nanowire boundary scattering conditions and other nanostructural efforts could be considered separately. Final results show that heterostructures and nanovoided structures offered the greatest improvements to electrical vs. thermal conductivity within the constraints of the simulation environment, and should be the focus of experimental research using the Al:ZnO material system provided that the materials could be readily synthesized. These observations are consistent with results published for other material systems[134]. Unfortunately, simulation limitations in structure size necessitated that the feature sizes in the modelled voided and heterostructured materials be less than those reproducible using established ZnO electrochemical growth methods.
2.3. Comparison and Summary of ZnO Nanostructures

Despite this acknowledgment, these structures were selected for experimental investigation. If voids and heterostructures can be produced with larger feature sizes, reducing the feature size using the electrochemical method to more closely match the modelled results is a potential subject for future work.
Chapter 3

Experimental Growth and Release of Al:ZnO

Based on the work in Chapter 2 and the work of others, Al:ZnO materials with nanovoids and heterostructural features were selected for electrochemical growth toward realizing a higher efficiency Al:ZnO thermoelectric material. Before considering the introduction of nanostructural features, suitable Al:ZnO films first had to be synthesized. Existing experimental literature on Al:ZnO focused exclusively on thin film growth of Al:ZnO for durations under two hours. The resulting film thicknesses were typically under 10\(\mu\)m, which, though feasible as a thermoelectric material, adds significant complexity to the design of the module and interface due to the increased relative effects of interface and other material layers in the module. To reduce the influence of interface layers, increase the accuracy of the thermoelectric film measurements, and simplify the measurement procedure by increasing mechanical strength of the films, thicker, higher quality, Al-doped ZnO films first had to be produced. The films would also have to be removed from the substrate to allow access to both sides for the purpose of thermoelectric characterization and integration into a thermoelectric module. Optimal growth conditions for long duration growth were experimentally explored, as were different methods for detaching the ZnO from the growth substrate.

Testing yielded that a vertically oriented-slide, situated in the centre of the solution (at least 1 cm from the base of the beaker) without stirring yielded the best results. Further discussion on these and other ZnO growth considerations not discussed in this chapter can be found in Appendix A.2.

Each section includes a literature review and separate equipment and methodology to introduce information and procedures specifically appropriate to the problem.
3.1 Equipment and Methodology

A potentiostat was constructed using an Agilent 34401A digital multimeter, a Keithley 2601 SourceMeter, LabView, and a GPIB network. The potentiostat was capable of both potentiostatic and galvanostatic deposition while also supporting two and three electrode configurations. In a potentiostatic mode, the applied voltage was adjusted to maintain the desired reference potential using a proportional-integral-derivative (PID) control loop. The experiments were conducted on a Fischer Scientific hotplate using a thermocouple for temperature regulation. Experiments involving small quantities of liquid (<30 mL) were placed within a hot water bath on the hotplate to improve temperature regulation. Charge transferred was monitored using a LabView project and depositions were configured to terminate once the desired electronic charge exchange had occurred. For more details on the LabView project, see Appendix E.

The reference electrode (Sigma Aldrich Z113085-1EA) used was an Ag/AgCl refillable, medium flow electrode containing saturated KCl. Working electrodes of copper, aluminum, platinum, zinc, and gold were all used throughout the experimental work. Platinum wire (99.99% pure) and zinc bars (99.9% pure) were acquired from Sigma Aldrich. The growth solution was composed of >99% pure Zn(NO$_3$)$_2$·6H$_2$O (Sigma Aldrich 96482-500G, with trace chloride and sulphate ions) and 99.997% pure Al(NO$_3$)$_3$·9H$_2$O (Sigma Aldrich 229415-10G) when doping was necessary. Distilled water from the same source was used in all experiments. The substrates were either indium tin oxide (ITO) on glass or gold (1000 Å) on chromium (50 Å) on glass wafers from EMF Corporation (CA134). Adhesive copper tape was used to connect the electrodes to wires leading to the potentiostat, and polyimide tape (3M 1205-series) was used in solution for any required masking.

At high temperatures, the experimental apparatus lost water due to evaporation. To compensate, a solenoid-actuated, DI water cistern was constructed above the hotplate, controlled by the LabView potentiostat software, that released solution (either DI water or DI water with dopant chemicals) into the growth beaker every 2.5 minutes to maintain a consistent water level.

A simple diagram of an electrochemical apparatus is shown in Figure 1.4. Specific details regarding probe spacing, solution concentrations, and analytes can be found in each subsection. The final apparatus for depositing Al:ZnO films used in thermoelectric characterization (Chapter 4) was a two electrode galvanostatic apparatus described in Section 3.4.1.

X-ray Diffraction (XRD) measurements were conducted using a Rigaku
3.2 Counter Electrode Selection

Multiflex XRD equipped with a Cu long fine focus and Cu Kα1+2 bandpass graphite monochromator at 40 kV acceleration potential and 20 mA emission current. Scanning Electron Microscopy (SEM) was used to produce microscopic images of materials surfaces. The images were recorded using an Hitachi S3000N VP-SEM at either 15 kV or 20 kV.

Energy-dispersive x-ray spectroscopy (EDX) measurements were performed using an Hitachi S3000N VP-SEM at 15 kV. Unless otherwise indicated, EDX measurements were performed in beam scanning mode where counts were collected over a five minute period. Quantitative values were calculated through automatic peak selection, manual trimming false peaks, and applying the Lorimer-Cliff method with ZAF correction using default k factor calibration coefficients\[154, 155\]. Reference ZnO powder (Sigma Aldrich) was used to verify the calibration of the instrument, yielding a ZnO molar ratio average of 49.03% to 50.97% with a standard deviation of 4.1%. Uncertainty reflected in EDX measurements in this work represents variation in multiple consecutive measurements, not overall measurement error, which should be taken to be 5% in the worst case. An example energy spectrum of a galvanostatically grown, Al-doped, chloride contaminated Al:ZnO thin film is shown in Figure 3.1. There are no obvious peaks not already attributed to the labeled elements. The count intensity and spacing between the aluminum and chloride peaks also facilitates higher resolution and accuracy measurement of these elements as there is no overlap in energy.

3.2 Counter Electrode Selection

The first consideration involved the examination of the counter electrode. Earlier publications involving the growth of ZnO using Zn(NO$_3$)$_2$ used zinc sheets as the counter electrode in the deposition to maintain availability of zinc ions during the process \[72, 81, 88\]. Although some modern research continues to use Zn sheets \[85, 156, 157\], many other researchers have switched to inert counter electrodes composed of platinum or graphite \[77–80, 83, 84, 86, 89\].

The risk of using an inert electrode for thicker film ZnO deposition based on Zn(NO$_3$)$_2$ is apparent from the electrochemical equations. Many papers describe the half cell reaction equation as similar to \[40, 77, 80, 82, 84, 89\]:

\[
\text{Zn}^{2+} + \text{NO}_3^- + 2\, \text{e}^- \rightarrow \text{ZnO} \downarrow + \text{NO}_2^-
\] (3.1)

Equation (3.1) neglects the ratio of usage of zinc and nitrate ions during
3.2. Counter Electrode Selection

Figure 3.1: Example EDX spectrum of a galvanostatically grown, Al-doped (5 µmol/L growth solution concentration), chloride contaminated Al:ZnO thin film.

the growth process, discussed by Marotti et al. and shown here [87]:

\[
\text{Zn(NO}_3\text{)}_2 \rightarrow \text{Zn}^{2+} + 2 \text{NO}_3^- \quad (3.2)
\]

\[
\text{NO}_3^- + \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{NO}_2^- + 2 \text{OH}^-
\]

\[
\text{Zn}^{2+} + 2 \text{OH}^- \rightarrow \text{Zn(OH)}_2 \rightarrow \text{ZnO} \downarrow + \text{H}_2\text{O} \quad (3.4)
\]

The overall reaction can be described as:

\[
\text{Zn(NO}_3\text{)}_2 + 2 \text{e}^- \rightarrow \text{ZnO} \downarrow + \text{NO}_3^- + \text{NO}_2^-
\]

The significant difference between (3.1) and (3.5) is in the inclusion of the remaining \(\text{NO}_3^-\) ion for every \(\text{Zn}^{2+}\) consumed by the reaction, which causes zinc ions within the growth solution to be consumed more rapidly than nitrate ions. Unusual effects such as extremely thin films during depositions
3.2. Counter Electrode Selection

at high potentials using inert electrodes have been reported, with the formation of hydrogen bubbles coating the surface of the film being cited as the cause [84]. The half cell reaction occurring at an inert counter electrode is:

\[ 2 \text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^- \] (3.6)

which is significantly different from the reaction at a zinc counter electrode:

\[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^- \] (3.7)

Note that it is also possible in both cases for hydrogen ions to form into hydrogen gas at the working electrode, although this is much more probable under acidic conditions.

The effect of Zn\(^{2+}\) reduction on ZnO film quality using a NO\(_3^-\) system was examined by comparing films grown using an inert platinum counter electrode with those grown with a zinc metal counter electrode. Experiments were performed at different temperatures, applied potentials, stirring rates, and beaker sizes.

3.2.1 Experimental Methods

The experiments were performed with either 20 mL or 100 mL of 0.1 M Zn(NO\(_3\))\(_2\)·6H\(_2\)O solution in 30 mL and 140 mL beakers, respectively. A standard three electrode potentiostatic set up was used, with a gold-plated glass working electrode (1000 Å gold on 50 Å chromium from EMF Corporation, 2.54 cm×7.62 cm total area, 2.54 cm×3 cm used), Ag/AgCl saturated KCl reference electrode, and either platinum wire or zinc rod (99.9% pure) counter electrode. The working and counter electrodes were 2 cm apart with the reference electrode within 1 cm of the working electrode. All voltage are expressed vs. Ag/AgCl. The growth solution was kept at 75 °C, measured by both thermocouple and glass thermometer, although solutions ranging from 65 °C through 85 °C were tested and were found to present the same trend. Reported results were based on experiments with a 250 RPM stir rod, although experiments without the stirring effect showed the same characteristics at lower current densities. Gold coated slides, used as zinc oxide deposition substrates, were washed with distilled (DI) water, acetone, methanol, and DI water again prior to use. The active region for deposition was masked using polyimide tape, which was experimentally determined not to significantly impact deposition results.

pH measurements were made with BDH35309.606 (VWR International) full range pH test strips with values recorded 10 seconds after removal from
3.2. Counter Electrode Selection

the growth solution to maximize consistency. Substrates were left in the growth solution after the completion of the electrodeposition process to cool gradually and prevent fracturing. Cooled films were rinsed thoroughly with DI water and left to air dry.

3.2.2 Single Potential Deposition

To confirm the persistence of evolved hydrogen ions in the growth solution, two identical film depositions of 13.3 C/cm² were performed at a range of potentials \( V_{\text{set}} = -1.0 \text{ V}, -1.1 \text{ V}, \text{ and } -1.2 \text{ V} \) in 20 mL beakers. Using the platinum counter electrode, available Zn²⁺ was reduced faster than NO₃⁻, encouraging the persistence of H⁺ ions from the counter electrode and a corresponding drop in pH as shown in Figure 3.2. A drop in solution pH is seen for all three deposition potentials, with stronger potentials yielding a lower overall pH at the conclusion of the experiment. The plateau is likely caused by the preferential formation of hydrogen gas at the working electrode. Bubbles were also seen forming rapidly at both electrodes later in the experiment.

A test using 100 mL showed a similar trend with a more gradual decrease in pH terminating at 4.1 after 75 minutes. The gradual increase in pH seen in the zinc counter electrode deposition is the consequence of hydroxyl ion formation within the solution. The presence of nitric acid was specifically tested by adding copper shavings into the growth media after the conclusion of the experiment and witnessing a slight blue shift in colour of the solution. Resulting film thickness was negligible (1 µm) for the platinum-grown samples and varied from 4 µm to 15 µm for the zinc-grown samples. The plateauing effect limiting the further acidification of the solution to approximately pH = 4 was likely due to reaction kinetics favouring the production of hydrogen gas over increased hydromium production in the solution.

H⁺ and oxygen gas are formed by electrolysis at the counter electrode (anode). A test enclosing the platinum counter electrode within a glass enclosure with a 1 mm² outlet was performed. The same reduction in solution pH was observed, but the drop in pH occurred at a slower rate, adjusted for current. The addition of the glass enclosure reduced the Faraday efficiency of the reaction by limiting mass transport and increasing the concentration of H⁺ immediately around the platinum electrode. Once the solution pH stabilized, it reached the same pH shown in Figure 3.2. Tests without the glass enclosure also do not run at perfect Faraday efficiency, with the voltage applied to the anode being adjusted by the potentiostat controller to prioritize a constant potential between the cathode and the surrounding solution.
3.2. Counter Electrode Selection

Figure 3.2: pH of 20 mL, 0.1 M Zn(NO$_3$)$_2$ solutions grown on 2.54 cm $\times$ 3.1 cm of exposed gold-coated glass using different counter electrode materials where a) shows pH as a function of deposition time and b) shows pH as a function of total applied charge. Uncertainty in pH measurement is $\pm$0.3.

rather than minimize overpotential for the hydrolysis reaction.

The current vs. time plot is shown in Figure 3.3. Whereas both depositions begin with the same trend, as the pH dropped in the solution with the platinum counter electrode, the current increased and stabilized, indicating gradual damage to the existing very thin film and no additional deposition. Oscillation in the current when using the platinum electrode could be due
3.2. Counter Electrode Selection

to bubble formation which was visible later in the experiment. The decreasing current of the deposition involving the zinc counter electrode is due to increasing resistance of the ZnO film, and is consistent with the growth of a good quality film.

![Graph](image)

Figure 3.3: Deposition current density of 20 mL, 0.1 M Zn(NO$_3$)$_2$ solutions grown using different counter electrode materials at a $V_{set} = -1.2$ V. Growth conditions were otherwise identical to those in Figure 3.2.

Samples grown at ($V_{set} = -1.2$ V) with different electrodes were also tested for their structural properties. SEM images of the surfaces of two films grown with inert and zinc counter electrodes are shown in Figure 3.4. A clear difference in surface morphology is visible, with the zinc-grown sample much more consistent with the results of others [72, 87, 88, 156]. It is also clear that the Pt-grown film is very thin and difficult to distinguish from the substrate (bottom of the image) when compared to the Zn-grown film. Tests were also performed with samples immediately removed from solution after the deposition was complete. These tests showed a slightly thicker film of similar surface morphology to Figure 3.4, indicating that further dissolution of the ZnO film occurred in the 20 mL beaker after the 3 hour deposition at $-1$ V vs. Ag/AgCl completed. Films removed immediately were still morphologically different in appearance than films grown with Zn counter electrodes, appearing darker and inconsistent. XRD data shown in Figure 3.5 similarly shows highly crystalline growth along $\langle 002 \rangle$ with the zinc-grown film and greater variability in growth orientation, apparent by visible peaks along $\langle 100 \rangle$ and $\langle 101 \rangle$ with the platinum-grown film. Films grown using inert electrodes for long durations were also visibly discoloured.
3.2. Counter Electrode Selection

3.2.3 Multiple Potential Deposition

The effect of zinc exhaustion was also explored at different deposition potentials using zinc counter electrodes. Figure 3.6 shows the deposition currents for depositions at \( V_{\text{set}} = -1.10 \, \text{V}, -1.05 \, \text{V}, \) and \(-1.00 \, \text{V} \) where \( -1.00 \, \text{V} \) is typically used in high quality ZnO growth \[77, 81, 83, 86\]. Each curve represents 1.3 C/cm\(^2\) of charge transferred. The dehydration of Zn(OH)\(_2\) into ZnO as shown by (3.5) is rate limited, allowing an increased rate of Zn\(_8\) and Zn(OH)\(_2\) integration into the film \[156\].

Figure 3.7 shows a single growth using a platinum electrode and 100 mL beaker at gradually increasing potentials. At potentials weaker than \( V_{\text{set}} = -1.0 \, \text{V} \), there is a small drop in pH as very little Zn\(^{2+}\) is consumed. At potentials stronger than \( V_{\text{set}} = -0.95 \, \text{V} \), the drop in pH is quite sudden and corresponds to a rapid increase in current density as zinc ions are strongly involved in the reaction. 2.67 C/cm\(^2\) of charge was deposited without the
3.2. Counter Electrode Selection

Figure 3.5: XRD measurements of films grown using either zinc or platinum counter electrodes under otherwise similar conditions. Counts have been normalized by intensity of (002) crystal orientation. The peak near scattering angle 38° is due to the gold substrate beneath the film. No unexpected out-of-band spikes were noted from 0-90°.

pH dropping below 5, which has been determined as a critical pH below which film growth is significantly inhibited despite high deposition current densities. After exposure at pH below 5 for 1.5 hours, the appearance of the surface of the film turned brown, although it still retained sufficient thickness and electrical resistance to indicate that exposure to the low pH did not dissolve much of the good quality film deposited earlier in the process.

3.2.4 Summary of Counter Electrode Effects

Under all test conditions, the zinc counter electrode provided a pH neutral solution that yielded high quality ZnO films with high transparency and ⟨002⟩ crystallographic alignment. When an inert counter electrode was used, a reduction in the solution pH was measured during all growth conditions, with pH dropping more rapidly with increased applied growth potential. Hydrogen ions formed at the counter electrode remained in the solution due to the ratiometric exhaustion of zinc ions, forming an acid that inhibited film
3.3. Reference Electrode Effects

Figure 3.6: Deposition currents of 100 mL, 0.1 M Zn(NO\textsubscript{3})\textsubscript{2} solutions grown using zinc counter electrodes at different reference potentials (V\textsubscript{set}). Normalization currents (A\textsubscript{0}) used are 19.6 mA, 21.2 mA, and 22.0 mA for V\textsubscript{set} = −1.10, −1.05, and −1.00 V, respectively.

growth below pH = 5, disrupted aligned crystal growth, and discoloured the surface of the film. Tests also showed that V\textsubscript{set} = −1.0 V, which is commonly used in ZnO growth, is at the inflection point where a small increase in potential magnitude can very rapidly decrease the pH of the solution. For long term, high quality, or highly doped growth, or for growth that can preserve the integrity of the growth solution for reuse, inert electrodes should not be used.

3.3 Reference Electrode Effects

The effects of the reference electrode on the quality of the film must be considered for long depositions. In most cases, thin ZnO films are produced potentiostatically over short durations of less than 2 hours using an Ag/AgCl reference electrode to maintain the desired applied electrochemical potential\cite{1, 40, 77, 89, 156}. ZnO growth under these conditions has yielded thin films and nanostructures with desirable optical and crystallo-
3.3. Reference Electrode Effects

Figure 3.7: Deposition pH and transferred charge of a 100 mL, 0.1 M Zn(NO₃)₂ solution grown using a zinc counter electrode with potential \( V_{\text{set}} \) varying throughout the deposition. Uncertainty in pH measurement is ±0.3.

graphic properties. As the film grows in a potentiostatic configuration, a rapid decay of deposition current provides a natural limit to film thickness as the electric resistance of the film increases with thickness[1]. Galvanostatic growth of zinc oxide enables the growth of films exceeding 50µm in thickness but requires long growth durations, rendering the films more susceptible to impurities in the growth solution. Examined in this section is the influence of chloride on ZnO thick film growth with deposition time up to and exceeding 11 hours.

The effect of chloride in electrochemically deposited zinc oxide nanostructures has been examined[45, 46]. Xu et al. determined that the addition of 0.06 mol/L chloride to a 0.05 mol/L Zn(NO₃)₂ solution forms interconnected, stacked ZnO platelets rather than rods on an indium tin oxide (ITO) substrate[45]. Cui et al. concluded that adding ammonium chloride to the growth solution reduces growth along the wire axis of ZnO nanowires while enhancing their radial growth and reducing optical transmission[46]. In both cases the amount of chloride was carefully controlled at the beginning of the deposition. A study on the effect of chloride on ZnO thick films
3.3. Reference Electrode Effects

electrochemically grown using Zn(NO$_3$)$_2$ has not been performed, nor have the implications of chloride leakage from Ag/AgCl electrodes on ZnO films been reported in detail.

3.3.1 Experimental Methods

All experiments used 100 mL of solution within a 150 mL beaker. The solution contained 0.1 M Zn(NO$_3$)$_2$·6H$_2$O with each experiment using distilled water from the same source. A standard three electrode configuration was used for all experiments consisting of a 99.9% pure Zn metal rod counter electrode, Ag/AgCl medium flow, saturated KCl reference electrode, and Au/Cr glass slide working electrodes. The working electrode and counter electrode were 6 cm apart with the reference electrode within 2 cm of the working electrode. Deposition occurred on gold and was masked using polyimide tape to isolate a deposition area of 1.0 cm×1.0 cm. Deposition temperature was maintained by thermocouple control at 80°C. Gold slides were rinsed with DI water prior to use, and all deposited films were left in the growth solution as the solution cooled after deposition to minimize thermal stress. Unless otherwise indicated, samples were grown galvanostatically at 1 mA/cm$^2$ until 40 C/cm$^2$ of charge was transferred, requiring approximately 11 hours of growth time.

Resistance measurements were taken using a two probe, IV curve method where a 3 mm diameter drop of eutectic GaInSb was used as one electrode and the gold substrate beneath the film was used as a second electrode. The contact angle between the bead and the ZnO film surface was similar with all samples. Resistance was measured through the film rather than along the surface. All resistance data indicated herein results from a linear fit of the resulting IV curve when sweeping the applied potential from −2 V to 2 V. Since measured resistance values are two orders of magnitude greater than short circuit resistance, cable losses are neglected. At least three complete measurement sets were made per film with a step resolution of 0.02 V and 5 s between steps to allow time for settling. A Keithley 2601a Source Meter was used for all measurements.

3.3.2 Results and Discussion

Refillable, metal-ion reference electrodes, such as Ag/AgCl and saturated calomel electrodes (SCE), use a porous plug to allow ionic transfer between the growth solution and the reference electrode. The solution within an Ag/AgCl electrode is ideally saturated KCl that will very slowly drain into
Reference Electrode Effects

the growth solution depending on the flow rate of the electrode. Higher flow rates provide for better ion exchange which allows faster response to changes in potential within the growth solution and greater measurement stability at the cost of more frequent electrode refills and contamination of the test solution. A saturated KCl, medium flow Ag/AgCl electrode with a measured flow rate of 127 \( \mu \text{L/hour} \) (445 \( \mu \text{mol/hour Cl}^- \)) was used for the experiments reported herein. All experiments involved ZnO growth on a gold substrate.

Both galvanostatic and potentiostatic experiments were conducted to confirm repeatability of the results. Potentiostatic films grown for short durations of under 2 hours demonstrated optical and morphological characteristics similar to other published films regardless of the presence of a Ag/AgCl electrode\[85, 156, 157\]. The potentiostatic deposition process begins at a high current density which diminishes rapidly within the first 15 minutes of the deposition\[1\]. The low estimated Cl\(^-\) concentration of 9 mmol/L within the solution after 2 hours combined with the very low current density of the deposition does not significantly impact the quality or character of the ZnO film.

The impact of Cl\(^-\) impurity within galvanostatically grown ZnO is much more significant than three electrode potentiostatically grown ZnO due to a higher, sustained current density that does not decrease with increasing film resistance. Galvanostatic growth maintains a constant current density that allows the reference potential to increase in order to maintain a constant applied current. Since the deposition current density is constant throughout the entire deposition and the deposition process can take a substantial amount of time, integration of Cl\(^-\) into the film will occur throughout the deposition process, including the later stages, when the concentration of Cl\(^-\) in the solution is significantly higher.

3.3.2.1 Chloride Concentration in ZnO

At the conclusion of an 11.1 hour deposition, 40 C/cm\(^2\) of charge was transferred at 1 mA/cm\(^2\) over 1.0 cm\(^2\), and the reference electrode raised the Cl\(^-\) concentration in the solution to 49 mmol/L, a concentration similar to that used by others for intentionally integrating Cl\(^-\) into ZnO\[45\]. Chloride concentration within the grown films was characterized using energy-dispersive x-ray spectroscopy (EDX) where chloride content was compared to zinc and oxygen within the film. EDX measurements of the completed films showed that films galvanostatically grown without a reference electrode had a chloride molar concentration of under 0.5%, within measurement error. Films
3.3. Reference Electrode Effects

grown under identical conditions with a reference electrode had a Cl\textsuperscript-- molar concentration of 4.5 \pm 0.5\% measured at the surface of the film, and films grown with a reference electrode at three times the speed (3 mA/cm\textsuperscript{2}) had a molar concentration of 1.5 \pm 0.5\%. Film thickness measurements provided a film thickness independent of chloride concentration of 45 \pm 5 \textmu m. Based on film thickness and mass measurements, an estimated 270 \pm 6 \textmu mol of ZnO was deposited for every 11.1 hour, 40 C/cm\textsuperscript{2} deposition. The amount of chloride absorbed for films deposited at 1 mA/cm\textsuperscript{2} was 12 \pm 4 \textmu mol, indicating that not all chloride was absorbed into the film.

The integration of chloride into the film as a function of depth was studied for the first half of the film. Morphological changes approximately 22 \textmu m from the base of the film prevented an accurate analysis of the cross section of the upper half of the film. The results are shown in Figure 3.8. The limitations of EDX, particularly when studying small concentrations of an element through the cross section of a film, restrict the quantitative conclusions that can be drawn from this figure. Qualitatively, a clear trend is visible from the onset of the deposition to the conclusion of the plot, representing 5.6 hours of growth. A slight increase in chloride concentration near 18 \textmu m also corresponds to a change in structural morphology where the

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Figure 3.8: EDX measurements performed at 15 kV on the cross-section of a ZnO film. EDX measurements were performed as discussed in Section 3.1 except for the beam mode which was set to point to increase spatial resolution. At least three samples were taken at different points throughout the film to determine the standard deviation as shown by the errors bars.
otherwise contiguous ZnO crystal begins to transition into larger platelets.

### 3.3.2.2 Crystallinity of ZnO

XRD measurements of representative galvanostatically grown films with and without a reference electrode are shown in Figure 3.9. The film grown with the reference electrode presented many additional peaks not attributable to either gold or ZnO. The additional peaks were not identical for every sample, but generally included a combination of \(2\theta = 11.7^\circ\) and \(28.6^\circ\), with smaller peaks at \(23.3^\circ\), \(30.9^\circ\), \(31.9^\circ\), \(33.0^\circ\), \(35.0^\circ\), \(49.0^\circ\), and \(50.3^\circ\). These peaks are consistent with the presence of AgCl and other Cl-based crystals within the film. Samples grown without the reference electrode in otherwise identical conditions only presented peaks corresponding with ZnO and Au, and also indicated favourable growth along \(\langle 002 \rangle\) as only the \((002)\) peak was visible in the XRD spectrum.
Figure 3.9: XRD results comparing peaks of a ZnO film grown with and without an Ag/AgCl reference electrode over 11 hours. The inset shows higher resolution results from $2\theta = 30^\circ$ to $38^\circ$ which is the region of greatest interest for assessing the crystallinity of ZnO film. Crystal orientations apply to ZnO unless indicated otherwise.
3.3. Reference Electrode Effects

3.3.2.3 Morphology of ZnO

SEM measurements were taken of galvanostatically grown films produced at 1 mA/cm² and 3 mA/cm² involving 40 C/cm² of charge transfer with and without a reference electrode. The SEM measurements are shown in Figure 3.10. The surface morphology of the films grown with and without the electrode are very different, with the films grown with the reference electrode showing increased surface roughness and less consistency across the surface. Figure 3.10h is an example of the surface structure most commonly found in potentiostatically grown films using an Ag/AgCl reference electrode as reported by others[72, 89].

![SEM results taken at a 45° angle showing low (a,c,e,g) and high magnification (b,d,f,h) comparisons of ZnO films galvanostatically grown at 1 mA/cm² (a,b,e,f) and 3 mA/cm² (c,d,g,h) until 40 C/cm² of charge had exchanged. Films in the top row were grown without an Ag/AgCl reference electrode, whereas films in the bottom row were grown with an Ag/AgCl reference electrode.](image)

The impact of the chloride on the film is also visible through optical microscopy. Higher concentrations of chloride render the film visibly grey and translucent; the surface also grows rougher with large crystals visible without microscopy. Optical microscopy photographs from two films galvanostatically grown with and without an Ag/AgCl electrode are shown in
Figure 3.11. The film grown without the reference electrode is optically transparent and very smooth, showing the gold substrate beneath the film.

Figure 3.11: Optical microscope images using yellow light to facilitate qualitative contrast between ZnO film crystallinity and yellow light transmission. Both ZnO films were galvanostatically grown a) using an Ag/AgCl reference electrode and b) without using a reference electrode. The chloride-contaminated film (a) appeared optically grey, translucent, and non-homogenous when visually compared to the film grown without the reference electrode.

3.3.2.4 Resistance of ZnO

Resistance measurements of galvanostatically grown films were completed on several films grown both with and without a reference electrode. All films were otherwise grown under identical conditions with measured thicknesses of $45 \pm 5 \mu m$ and cross-sectional areas $1.0 \text{ cm}^2$. The resistance of films grown with the reference electrode varied significantly from $20 \text{k}\Omega$ to $2 \text{M}\Omega$. Films grown without the reference electrode provided a consistent resistance of $1000 \pm 200 \Omega$. The same bead of InGaSn was used to test each sample to maximize the consistency of the resistance measurements to maximize consistency in results. Annealing at $200^\circ\text{C}$ for 2 hours did not affect the resistance of the chloride contaminated films, although discolouration of the film did occur. The current-voltage (IV) curve of the chloride-contaminated film was measured to be highly non-linear when compared with films grown without the reference electrode.
3.3.3 Summary of Reference Electrode Effects

Using a saturated KCl Ag/AgCl reference electrode when growing ZnO with Zn(NO$_3$)$_2$ necessitates an exchange of chloride ions into the growth solution. Potentiostatic deposition, which is self limited by the decay of the deposition current, is not significantly impacted, however some small amount of Cl$^-$ is incorporated into the film and this has a measurable effect on the crystallinity and morphology of the ZnO. Galvanostatic growth of thicker films is more significantly impacted by Cl$^-$ leakage due to the extended durations of the deposition and the high, sustained current density. Chloride is detectable in the films at thicknesses of only 5µm although effects on morphology are not apparent until chloride molar concentration exceeds approximately 1%. The variations in crystallinity, morphology, opacity, electrical resistance, and surface roughness are quite severe, with films grown using an Ag/AgCl reference electrode showing generally less desirable characteristics. If potentiostatic growth of ZnO is required then Hg/HgO or Hg/HgSO$_4$ electrodes should be considered.

3.4 Growing and Characterizing Al:ZnO Films

Aluminum can be integrated into the film in a variety of ways\[64, 65, 67, 68\]. The preferred type of integration involves substitution doping whereby zinc ions are replaced by aluminum ions in a predominantly ZnO crystal lattice. The replacement results in localized distortions in the lattice structure and serves to n-type dope the material, in some cases yielding extremely high electrical conductivity exceeding 2000 S/cm\[54\]. A type of integration which is common in hydrothermal and electrochemically deposited films involves the absorption of a Zn-Al double layered hydroxide, or the absorption of Zn(OH)$_2$ and Al(OH)$_3$ nanoparticles directly into the film\[67, 156\]. The absorption of hydroxides reduces film electrical conductivity and cannot be considered a type of doping. In addition to aluminum doping, oxygen doping of ZnO by varying the applied electrochemical potential can also have dramatic effects on the electrical properties of the film\[156\]. Aluminum doping of ZnO has been demonstrated at Al:Zn ratios of 0.1:1 (10% substitution), although 2% is nominal for Al:ZnO thermoelectric materials\[44, 52, 53, 62–64\].

An important limitation in the available literature for producing Al:ZnO electrochemically involves the study of Al-doping in thicker (>20µm) Al:ZnO films based on the nitrate growth system. Existing experiments generally limit growth times to under 2 hours\[45, 46, 59\] and focus primarily
3.4. Growing and Characterizing Al:ZnO Films

on potentiostatically grown films, which are practically restricted in their growth thickness due to long growth times resulting from decaying deposition current and contamination as the film thickens[1][158]. Thicker films are desirable for some applications, such as thermoelectrics, where thicker materials can more easily be integrated into modules, and thickness can be used to regulate thermal power absorption of the device. These thicker films are best grown galvanostatically, with applied current affecting both ZnO film characteristics[156] and Al/Zn ion selectivity during growth[58]. In this section, the feasibility of growing low resistance, Al:ZnO thick films using a galvanostatic, nitrate-based electrochemical method is discussed.

3.4.1 Experimental Methods

All films were grown using an electrochemical galvanostatic growth method. 150 mL beakers containing 100 mL solutions of 0.1 M Zn(NO$_3$)$_2$ · 6 H$_2$O were placed on a standard hotplate with thermocouple control and set to 80°C. 99.9% pure zinc metal counter electrodes were used along with gold-plated glass slides. The working electrode and counter electrode were 6 cm apart with the reference electrode within 2 cm of the working electrode. The slides were masked with polyimide tape (3M 1205-series) to provide a deposition area of 1.0 cm × 1.0 cm and were washed using distilled water prior to beginning each experiment. An Ag/AgCl reference electrode (Sigma Aldrich Z113085-1EA) was used for voltammogram experiments but was not used for thick film growth in order to minimize chloride contamination within the grown films.

Al(NO$_3$)$_3$ was introduced into the growth solution at 2.5 minute intervals by solenoid-switched gravity feed from a 500 mL chemical cistern located above the galvanostat. The doping solution concentration within the cistern was selected to achieve the desired dopant concentration within the growth solution while concurrently replacing water lost due to evaporation. The cistern release period was chosen to allow absorption of available Al(NO$_3$)$_3$ and minimize the amount of distilled water added with each release to prevent sudden cooling of the growth solution. The valve was opened for 400-500 ms per cycle, representing approximately 1.8 mL of solution, depending on the dopant concentration used to adjust for variations in solution evaporation rate.

The growth solution was allowed to stabilize in temperature with the counter electrode in place. The working electrode was only added to the beaker after the latter had reached the desired temperature and the deposition could begin. The cistern was activated concurrently with the beginning
of the deposition. The deposition process for each film required slightly over 11 hours to grow a nominally 45 µm thick film with a total charge density transfer of 40 C/cm². Unless otherwise indicated, a constant deposition current density of 1 mA/cm² was used.

Film thickness was measured using both SEM cross-section measurements and a high resolution Nikon MM-400 optical microscope with good agreement. Photographs were taken with a standard optical microscope at 10× optical zoom. Resistance measurements were performed using the two probe method described in Section 3.3.1

3.4.2 Results and Discussion

3.4.2.1 ZnO Film Base Composition

As discussed in Section 3.2, the process of depositing ZnO from a Zn(NO₃)₂ solution involves two predominant steps: 1. Nitrate ions electrochemically break down into hydroxide ions. 2. The hydroxide formed at the working electrode then reacts with the Zn²⁺ in solution and thermally decompose into ZnO. The rate of the first reaction is largely governed by the applied electrochemical potential between the working and counter electrodes. The rate of the second reaction is largely governed by the temperature of the solution. A solution temperature of 80°C was selected due to its ubiquitous use by others performing a similar deposition [1, 77, 156, 159]. Deposition current densities ranging from 1.0 mA/cm² to 3.0 mA/cm² are equivalent to initial reference potentials of −0.90 V - −1.0 V vs. Ag/AgCl, with the latter potential being commonly used in nitrate-based deposition [72, 77, 156]. Films grown using various currents in this range were examined for their influence on the composition of an undoped ZnO film.

Films were grown at 1 mA/cm² and 3 mA/cm² under identical conditions until 40 C/cm² of charge had been transferred. As shown by Figure 3.12 the change in zinc to oxygen ratio within the film is quite small for the two different current densities. In both cases, the amount of oxygen within the film is greater than the 50% expected and shown by the ZnO reference samples (Sigma Aldrich 255750-100G). The additional oxygen in the film is likely due to excess Zn(OH)₂ stored in the film during deposition [156]. The introduction of aluminum dopant into the film by maintaining 5 µmol/L Al(NO₃)₃ in the growth solution displaces zinc atoms as desired, but otherwise does not significantly impact the ratio of zinc and oxygen in the film.

The film cross-section shown in Figure 3.13 is consistent with SEM images produced by others and presents a polycrystalline film consisting of
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Figure 3.12: Quantitative EDX results showing a molar concentration comparison between a commercially purchased ZnO reference powder and galvanostatically grown ZnO films prepared at different current densities and aluminum concentrations. EDX measurements were performed as described in Section 3.1. Error bars represent the maximum and minimum of at least three measurements across the surface of the material. Accuracy should be considered within 5%.

large segments of ZnO closely packed and oriented along the c-axis. The crystallinity of the ZnO is determined by XRD measurements where a growth preference along \(\langle 002\rangle\) is shown by Figure 3.14. Although some counts are detected at \(2\theta = 31.7^\circ\) and \(36.2^\circ\), representing growth along \(\langle 100\rangle\) and \(\langle 101\rangle\) axes, respectively, they are nearly within the noise floor of the measurement. There are no unidentified peaks on the XRD plot, which indicates that despite a long deposition time of 11 hours, the film is of high crystal purity. EDX measurements also did not indicate the presence of other unexpected, heavier elements within the film.

The average film thickness measured using both the SEM and microscope of samples grown at 1, 2, and 3 mA/cm\(^2\) were all 45 ± 5\(\mu\)m, with one side (closer to the bottom of the beaker during growth) up to 10\(\mu\)m thicker.
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Figure 3.13: 45° SEM cross-section of an undoped ZnO sample galvanostatically grown on gold at $I_{set} = 2.0 \text{mA/cm}^2$ for 5.5 h at $T = 80^\circ\text{C}$.

than the top of the film (edge of the masked region near the surface of the growth solution). The measured thickness is also approximately 50% larger than the theoretical thickness of 31.2 µm determined using Faraday’s Law. This sizable discrepancy further indicates the inclusion of zinc and oxygen in different, non-crystalline configurations within the bulk of the film. The extra volume is most likely water and Zn(OH)$_2$, supported by the oxygen concentration of the film being higher than the zinc concentration as shown in Figure 3.12.

3.4.2.2 Aluminum Absorption

The aluminum dopant was introduced at regular intervals into the growth solution. Aluminum ions electrochemically react with greater favorability to zinc ions in the range of interest as shown in Figure 3.15. The voltammogram analysis indicates that the aluminum ion reaction begins at potentials as low as $V_{ref} = -0.3 \text{V vs. Ag/AgCl}$ and remains dominant until $V_{ref} = -1.0 \text{V vs. Ag/AgCl}$. As the dopant concentration in the growth solution will be small relative to the zinc ion concentration, favourable Al$^{3+}$ reaction is desired. Although it is common in literature to introduce the desired dopant once at the onset of deposition, thicker film growth must accommodate for the
3.4. Growing and Characterizing Al:ZnO Films

Figure 3.14: XRD spectrum of ZnO and gold substrate showing high (002) (c-axis) orientation of the film.

effect of rapid Al\(^{3+}\) absorption. Figure 3.16 shows the measured reference potential of an Ag/AgCl electrode when drops of Al(NO\(_3\))\(_3\) are introduced to a Zn(NO\(_3\))\(_2\) growth solution during a galvanostatic ZnO deposition. The rapid drop in potential and its subsequent return to normal is a consequence of the appearance and rapid consumption of Al\(^{3+}\). Some of the aluminum is absorbed into the film, but the Al\(^{3+}\) ions also react favourably with OH\(^-\) produced by the decomposition of nitrate ions, yielding a white particulate, Al(OH)\(_3\), that precipitates out of the solution. The rate of reaction is dependent on the concentration of aluminum with the majority of Al\(^{3+}\) consumed within 2 - 10 minutes of introduction (10 - 1000 \(\mu\)mol/L).

A final deposition current density of 1.0 mA/cm\(^2\) was selected to maintain high electrical conductivity in the grown film and maximize electron mobility\(^1\)[56], while also encouraging aluminum absorption into the film\(^5\)[58]. Using Figure 3.16, an assumption is made that nearly all Al\(^{3+}\) is consumed 2.5 minutes after the previous drop of Al(NO\(_3\))\(_3\) is introduced into the growth solution for peak growth solution concentrations of approximately 10 \(\mu\)mol/L Al(NO\(_3\))\(_3\). The cistern solution Al(NO\(_3\))\(_3\) concentration is prepared to raise the concentration of Al\(^{3+}\) in the growth solution from zero to the indicated concentration with every refill. Approximately 450 mL of refill
3.4. Growing and Characterizing Al:ZnO Films

Figure 3.15: A plot showing voltammograms of 0.1 M Zn(NO$_3$)$_2$ and 0.1 M Al(NO$_3$)$_3$ taken on identical gold substrates and at identical temperatures of 80°C. Each test was performed three times consecutively with all six curves shown in the plot.

solution is required to complete an 11 hour deposition. Chemically stable polymer components were used in the cistern construction to maximize potency and stability of the dopant solution throughout the deposition. No precipitates were noted in the cistern during or after deposition experiments. Figure 3.17 shows quantitative EDX measurements of the molar ratio of aluminum atoms in grown films compared to oxygen and zinc atoms. The best fit line represents a logarithmic trend, suggesting that, under the conditions listed, the quantity of aluminum in the ZnO film is a logarithmic function of the concentration of Al(NO$_3$)$_3$ available in the growth solution.

Al(NO$_3$)$_3$ in the growth solution interferes with the formation of ZnO by reacting with hydroxide ions and precipitating them out of the solution. The resulting reduction in measured film thickness for a constant 40 C/cm$^2$ charge transfer is shown in Figure 3.18. The reduction in film thickness is due to the parasitic removal of electrochemically generated hydroxide by aluminum ions. A further constraint to applying Al(NO$_3$)$_3$ concentra-
3.4. Growing and Characterizing Al:ZnO Films

Figure 3.16: A plot showing the Ag/AgCl reference voltage response to the introduction of varying concentrations of Al(NO$_3$)$_3$. 100 µL to 1 mL volumes of Al(NO$_3$)$_3$ were introduced to a 100 mL solution of 0.1 M Zn(NO$_3$)$_2$ undergoing galvanostatic deposition at 1.0 mA/cm$^2$ to raise the solution concentration of Al$^{3+}$.

The composition of the Al(OH)$_3$ layer was confirmed through quantitative EDX measurements, which consistently indicated a molar ratio of one aluminum atom to three oxygen atoms. The layer forms later in the deposition as the amount of floating precipitate increases, and eventually begins to coat the surface of the ZnO, interfering with further growth by decreasing available surface area and blocking ion migration. The hydroxide layer does not bind to the surface of the ZnO and was removed through light physical abrasion and compressed gas. The hydroxide layer is very brittle and thin,
Figure 3.17: A plot showing quantitative EDX measurements of Al$^{3+}$ molar concentration within the film as a function of sustained dopant concentration within the electrochemical growth solution. The molar quantity of aluminum is compared to that of zinc, oxygen, and chloride also found in the film. The solid line represents a logarithmic fit.

readily fracturing into an insoluble powder.

Approximately 20% of the aluminum ions provided throughout the deposition are integrated into the film, with the remainder precipitating from the solution, forming a protective layer over the film, or remaining dissolved within the growth solution.

### 3.4.2.3 Dopant Integration

In an ideally doped material, the Al$^{3+}$ ions replace Zn$^{2+}$ ions in the ZnO crystal lattice, contributing electrons to the crystal and improving electrical conductivity. More commonly in hydrothermally or thermochemically deposited ZnO formed in the presence of hydroxide and aluminum ions, a hydroxide double layer is formed that replaces the preferred ZnO lattice\cite{64, 65, 67, 68}. It is clear that aluminum ions are interacting with hydroxide in the solution by the formation of a white precipitate that is only apparent when Al(NO$_3$)$_3$ is added to the solution. Higher integration of aluminum into the film also affects the visible properties of the film by
3.4. Growing and Characterizing Al:ZnO Films

Figure 3.18: A plot showing film thickness measurements as a function of sustained aluminum dopant concentration within the electrochemical growth solution. All films were grown at identical current densities of 1 mA/cm² for identical durations of 11.1 hours. The solid line represents a logarithmic fit.

Increasing its opacity and rendering the film optically grey as the total molar concentration of Al³⁺ in the film exceeds 1%. Further effects to the morphology and crystallography of the film are also measurable.

Figure 3.20 shows SEM images of ZnO film surfaces at increasing concentrations of Al³⁺. At low molar concentration of aluminum (<0.5%), the film forms large, highly oriented slabs. As the aluminum concentration increases, the slabs decrease in size and consistency, the film develops a nearly porous structure (1% molar concentration, 5 µmol/L used during growth), and, at concentrations approaching 2% Al³⁺, the film appears nearly amorphous at the surface. Despite the apparent change in morphology, the materials are optically similar and transparent at all tested concentrations. The contact angle and adhesion of a GaInSb drop does not change significantly with the surface morphology of the material. The roughness of the surface prevents adhesion and wetting by liquids with high surface tension.

The effect of doping on crystallinity was also examined using XRD analysis as shown in Figure 3.21. The impact of higher concentrations of Al(NO₃)₃ in the growth solution on the crystallinity of the resulting film is very small. Despite the significant morphological changes and the possible formation of
3.4. Growing and Characterizing Al:ZnO Films

Figure 3.19: 45° SEM images of an Al:ZnO sample grown with 30µmol Al(NO$_3$)$_3$ solution where a) shows both the ZnO film surface (below) and the layer of caked Al(OH)$_3$ (above), and b/c) shows closer images of the Al(OH)$_3$ layer.

A hydroxide double layer within the film, the overall bulk of the film remains highly oriented along (002) (c-axis). If the angular offset of each XRD measurement is carefully adjusted to align with the substrate gold peak (111) to compensate for subtle changes in film measurement parameters, a very close examination of the peaks of the ZnO (002) peak do show a change in crystal lattice $c$ parameter with the introduction of aluminum into the film. A change of 0.05° (average change in diffraction angle along ⟨002⟩) represents a contraction in $c$ of 0.1%. This contraction could be the result of substitution doping where the additional positive charge of the aluminum ion would attract the surrounding oxygen ions, or it could be the result of
3.4. Growing and Characterizing Al:ZnO Films

Figure 3.20: 45° SEM images of ZnO samples galvanostatically grown at \( I_{\text{set}} = 1.0 \text{ mA/cm}^2 \) with approximately a) no dopant, b) 1 \( \mu \text{mol/L Al(NO}_3\text{)}_3 \), c) 3 \( \mu \text{mol/L Al(NO}_3\text{)}_3 \), d) 5 \( \mu \text{mol/L Al(NO}_3\text{)}_3 \), e) 10 \( \mu \text{mol/L Al(NO}_3\text{)}_3 \), and f) 30 \( \mu \text{mol/L Al(NO}_3\text{)}_3 \).

a difference in internal stress within the film due to smaller crystal sizes with increasing aluminum integration. There were no detected variations in other peaks within the \( 2\theta = 1^\circ \text{ - } 90^\circ \) band. No peaks representing ZnAl\(_2\)O\(_4\), aluminum metal, or Al\(_2\)O\(_3\) were found.

Resistance measurements along the (002) plane through the thickness of the film were performed on a probe stand using a bead of GaInSb as the top electrode and gold substrate as the bottom electrode. Apparatus resistance was measured and removed from film resistance measurements. Resistivity, shown in Figure 3.22, was approximated by estimating droplet size and accommodating for film thickness. Both resistance and resistivity show very similar trends. As more aluminum is integrated into the film, the resistivity of the film drops, but not as quickly as would be expected for full substitution doping. Once the dopant concentration is sufficient to interfere with film growth (10 \( \mu \text{mol/L} \)), a new behaviour is observed where the resistivity is nearly constant. This latter behaviour is consistent with a reduced rate of aluminum uptake by the ZnO during growth at high concentrations of Al\((NO_3)_3\). In all cases, measured current vs. voltage (IV) curves were linear and intercepted 0 A. At least three samples were taken per film at different locations.

Although the drop in resistivity of the film with increasing aluminum indicates substitution doping, the gradual rate of change suggests that the aluminum/zinc substitution is imperfect. The integration of Al(OH)\(_3\) di-
3.4. Growing and Characterizing Al:ZnO Films

Figure 3.21: An XRD spectrum comparing 2θ angle of ZnO galvanostatically grown at $I_{set} = 1.0 \text{ mA/cm}^2$ with different concentrations of Al(NO$_3$)$_3$ with a) showing the primary range of interest for ZnO structures and b) emphasizing the slight difference in peak position between the doped films.
3.4. Growing and Characterizing Al:ZnO Films

Figure 3.22: ZnO film resistivity as a function of estimated Al(NO$_3$)$_3$ dopant concentration in the growth solution. Measurements represent c-axis resistivity.

rectly into the film is more probable.

3.4.2.4 Annealing

Low temperature annealing of the films was performed in air to explore the presence of hydroxide within the films and determine whether annealing could improve substitution doping in the films containing aluminum. Annealing was performed for 2 hours at 200°C in a forced air temperature chamber and 400°C on a covered hotplate. Within the first 30 minutes of annealing all tested films turned fully opaque and white, dissociating from the gold substrate, cracking and deforming (curving). All resulting films appeared identical, regardless of doping concentration, and fractured into pieces up to 0.5 cm$^2$ in size. Annealing began visibly affecting the film at temperatures as low as 60°C.

Additional resistivity calculations were performed on larger pieces of the films along ⟨100⟩. GaInSb was formed into two contacts on a glass slide and the pieces of fractured film were measured and then placed on the glass slide bridging the two GaInSb electrodes where additional eutectic liquid was added to form full contact with the edges of the film. Measurements
indicated a significant drop in electrical resistivity of all films, with the undoped film at $20 \pm 10 \, \Omega \text{cm}$ and other films annealed at $200^\circ \text{C}$ also providing a similar resistivity. Films annealing at the higher temperature, $400^\circ \text{C}$, demonstrated a higher resistivity of $200 \pm 50 \, \Omega \text{cm}$.

XRD analysis of the annealed films produced identical, but broader, peaks as those show in Figure [3.21]. The increased peak width can be attributed to the samples under study being curved by the annealing process.

The significant change in optical and electronic properties of the films after a low temperature anneal indicate that a significant amount of unreacted Zn(OH)$_2$ or Al(OH)$_3$ is still present in the film. The application of further heat prompts a thermal decomposition process but at such low temperatures the resulting products cannot effectively integrate into the existing ZnO lattice, causing deformation and fracturing of the film. Sintering at very high temperature would likely return the ZnO film to a more resistive, optically transparent state.

### 3.4.3 Summary of Al:ZnO Growth

The formation of thick film Al:ZnO was explored using an electrochemical nitrate system. A new growth methodology is presented where Al(NO$_3$)$_3$ is used as a dopant agent and is introduced into the growth solution gradually throughout the deposition to maximize doping consistency in the film. Films up to $45 \pm 5 \, \mu\text{m}$ are grown over 11 hour depositions with Al$^{3+}$ molar concentrations of up to 1.72% (Al$_{0.034}$Zn$_{0.966}$O) being realized. The influence of Al(NO$_3$)$_3$ concentration in the growth solution on film thickness was explored, where approximate concentrations above 30$\mu$mol/L precipitated sufficient Al(OH)$_3$ to significantly interfere with ZnO film growth.

ZnO crystal size and overall crystallinity for variably doped ZnO films was examined. The crystal size began dropping with dopant concentrations above 3$\mu$mol/L, demonstrating two contrasting dopant integration effects. Some substitution doping occurs, causing a shift in XRD (002) peak and a drop in film resistivity, but increasingly higher concentrations of Al$^{3+}$ in the growth solution interfere with monocrystalline ZnO growth, reducing the substitution doping effect, and integrating more Al(OH)$_3$ directly into and onto the film. Evidence supporting the integration of hydroxide into the films include 50% greater film thickness than electrochemically predicted based on charge transfer, chemical reactions at $80^\circ \text{C}$ after deposition completion and film drying, a higher measured percentage of oxygen to zinc within the grown films, and work by others on electrochemical and hydrothermal growth of ZnO drawing the same conclusion[67, 156].
3.5 Release of Films from the Substrate

Under no conditions was it possible to achieve the theoretical 2000 S/cm electrical conductivity reportedly possible for the Al:ZnO material system. The highest electrical conductivity was achieved at a growth solution Al(NO$_3$)$_3$ concentration of 30 µmol/L yielding 2.5 mS/cm prior to annealing. Low temperature annealing significantly improved the film electrical conductivity of all samples tested while concurrently rendering the films white, opaque, and structurally uneven.

3.5 Release of Films from the Substrate

In order to access both sides of the ZnO film for thermoelectric testing, the ZnO film must first be removed from the glass slide on which it was grown. A variety of methods were explored for gaining access to both sides of the film, with some discussed in Appendix A.3. Considering the utility of releasing a grown structure from a glass slide after undergoing a deposition procedure in solution, a versatile technique was developed to accommodate ZnO films and potentially some biological and MEMS devices as well by etching away the chromium layer that binds the gold layer of the substrate to the glass. This room temperature process consisting of non-toxic and optionally pH-neutral solvents presents a useful contrast to many other sacrificial layering techniques that require strong acids and bases, vacuum environments, or toxic chemicals to perform the etching process. Compatibility with solution-based material deposition further increases the utility of this method over using materials such as NaCl as a sacrificial layer.

Gold is commonly used in the fabrication of many microelectromechanical systems (MEMS) and other microscale and nanoscale devices. Its many uses derive from its high electrical conductivity, ductility, resistance to oxidation, comparative chemical inertness, biocompatibility, and special catalytic properties[160–164]. Gold is used as a substrate for the sputtering or electrochemical deposition of thin films[1, 165], MEMS structural components[163], and nanostructured materials[82]. Its special surface properties also make it an ideal material for biological cell adhesion[161, 166] and as a substrate for the deposition of evaporated nanoscale oxide structures[167].

Devices that use gold as the substrate are often based on gold-coated glass slides. These slides consist of a thin layer of gold, typically 100 nm - 1 µm thick, deposited on a 5 nm thick chromium adhesion layer initially evaporated on to the glass slide. These glass slides are used in applications such as microfluidics[168] and thin film thermoelectrics[1]. These and potentially other applications can benefit from lifting the gold and associated
3.5. Release of Films from the Substrate

structures from the glass slide using a process that does not physically or chemically damage the structure. When working with oxides or biological structures, it is particularly necessary to avoid strongly acidic and high temperature process steps.

A practical method for releasing the gold film and accompanying surface structure is the etching of the chromium (Cr) adhesion layer between the gold film and the glass substrate to release the gold, which has a low adhesion to glass.

3.5.1 Chemical Etching of Chromium

Chromium etching is typically performed using a mixture of nitric (HNO$_3$) or perchloric (HClO$_4$) acid and a strong oxidizer such as ceric ammonium nitrate (H$_8$N$_8$CeO$_{18}$)[169][171]. This method of chromium etching has several disadvantages, including the immersion of the device into an acidic and oxidizing bath, slow etching times, and high reagent cost. Tests using this prescribed formula were performed on ZnO samples grown on gold substrates as described in Section 3.2. Despite attempts to cover the ZnO layer, which is highly reactive to acid, using kapton tape and acrylic conformal coat, the etching dissolved the ZnO layer in every test. During the etching process, the gold became brittle and curled, creating small cracks that allowed the etching to contact the ZnO film, destroying the sample. After several attempts, chemical etching under extremely acidic conditions was halted.

3.5.2 Electrochemical Etching of Chromium

Conventional electrochemical chromium etching is generally performed in a low pH solution of sulphuric acid and is believed to follow one of many potential dissolution paths. Commonly described possibilities are[172]:

$$\text{Cr}(s) \rightarrow \text{Cr}^{2+} + 2e^-$$ (3.8)

or

$$\text{Cr}(s) + \text{H}_2\text{O} \leftrightarrow \text{CrOH}_{(ad)} + \text{H}^+ + e^-$$ (3.9)

$$\text{CrOH}_{(ad)} \leftrightarrow \text{CrOH}^+ + e^-$$ (3.10)

$$\text{CrOH}^+ + \text{H}^+ \rightarrow \text{Cr}^{2+} + \text{H}_2\text{O}$$ (3.11)

Both sets of equations describe a constant pH reaction where the acidity of the etching solution does not change. Similarly, no precipitates are
formed, and the free Cr\(^{2+}\) is deposited on the cathode throughout the experiment. Problematically, strong acids are still necessary for the reaction, limiting the potential applications of the technique.

A new approach was examined for releasing the gold thin film that addresses these issues by using a pH-neutral or basic electrochemical etching process to selectively dissolve the chromium.

### 3.5.3 Procedure and Equipment

The standard reduction potentials to dissolve chromium, ZnO, and gold in a pH neutral, room temperature solution are 0.91 V, −1.26 V, and −1.43 V, respectively\[173\]. These potentials allow for a preferential etch of chromium over ZnO and gold, which require a larger potential. Non-conductive materials such as insulators and many biological molecules do not participate significantly in the electrochemical etching process and must only tolerate phosphate or hydroxide ions in neutral or basic conditions. Strongly electrically insulating materials such as glass and polyimide tapes do not allow electrons from the working electrode to penetrate the surface and oxidize the material. Similarly, although many biological materials allow for ion exchange through a membrane, they do not act as high conductivity electron conduits that undergo oxidation when within an electrochemical bath.

#### 3.5.3.1 Slide Preparation

2.0 cm×1.5 cm gold-coated slides consisting of 1 mm glass, 5 nm of Cr as an adhesion layer\[174\], and 100 nm of Au as the substrate layer were acquired from EMF Corp (P/N CA134). Process characterization was performed using these blank gold slides with copper tape adhered at one end, protected with polyimide tape (3M 1205-series), acting as the wire to the potentiostat. Etching distance was measured by marking the glass on the rear of the slide with permanent marker and observing the regression of chromium throughout the etch.

Slides were separately coated and tested with 1.0 cm×1.0 cm segments of polyimide tape placed directly over the gold in the center of the slide and thin films of deposited ZnO. A diagram of the slide after ZnO deposition can be seen in Figure[3.23] Slides were prepared for 1.0 cm×1.0 cm (2.0 cm×1.5 cm slide) and 0.5 cm×0.5 cm (1.0 cm×1.0 cm slide) depositions of ZnO film. The films were grown using the methods described in Section[3.4].

All slides were rinsed briefly with distilled water using a spray bottle to remove any debris prior to performing the etching procedure.
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Figure 3.23: A sample configuration, not shown to scale. 2.0 cm x 1.5 cm gold coated slides were procured and then partially electrochemically coated with a 1.0 cm x 1.0 cm x 20 µm thick layer of ZnO or a 1.0 cm x 1.0 cm x 76 µm thick layer of polyimide tape. Copper adhesive tape, protected by polyimide, was used to electrically connect the slides to a potentiostat.

3.5.3.2 Solution Selection

Several solution ions were tested for their suitability. Preliminary testing showed that 0.1 M KCl etched both the gold and chromium layers equally, resulting in the destruction of the test film and surrounding material. Similar effects were also seen with 0.1 M Zn(NO$_3$)$_2$, although some selectivity for etching chromium preferentially to gold was apparent in that the gold film did not dissolve as rapidly. Other common ions, including sulphate, acetate, and cyanide were ruled out due to poor selectivity or undesirable environmental effects.[172, 175–178]. Both sodium hydroxide (NaOH) and phosphate solutions (Na$_2$HPO$_4$ and NaH$_2$PO$_4$) showed excellent selectivity for etching chromium without damaging the gold film.

3.5.3.3 Apparatus

A diagram of the electrochemical apparatus is shown in Figure 3.24. The apparatus required a standard potentiostat capable of providing a DC voltage, measuring current, and optionally displaying the solution potential relative to the cathode using a reference electrode. The same apparatus used for depositing the ZnO thin film was also used to release the gold and ZnO films from their substrates. The cathode was a conventional, reusable, 4 cm$^2$ copper strip for collecting the ionized chromium from the solution. Copper adhesive tape was used to attach both electrodes to the glass dish and connect them electrically to the potentiostat. A medium flow, Ag/AgCl reference electrode was also used, although precision potential control within
3.5. Release of Films from the Substrate

Figure 3.24: Schematics of the setup for etching the chromium from the slide and releasing the gold film. The optional reference electrode is not shown but would be located in close proximity to the glass slide.

the solution was not strictly necessary. A loop of polyimide tape secured the sample in the pyrex dish when required. For ZnO-coated samples in excess of 0.25 cm$^2$ in area exposed to the etching solution, submerging the sample gradually by periodically adding additional solution, as discussed in the following section, improves the yield of the etching process. A simpler procedure acceptable for bare or small (<0.25 cm$^2$), coated substrates allowed for mounting the device vertically on the wall of the dish and covering the entire substrate with etching solution at the onset of the experiment.

3.5.3.4 Procedure

The slide and solution was first prepared. Sufficient solution was necessary to cover the slide as mounted within the apparatus by the end of the etching process. When using a 300 mL, 90 mm diameter dish, 100 mL of solution is required.

Two separate procedures were employed depending on the coating of
3.5. Release of Films from the Substrate

the slide. For all slides except those coated with 1.0 cm × 1.0 cm of ZnO, the slide was aligned vertically along the side wall of the dish and the entirety of the etching solution was added at the beginning of the etch. For etching beneath ZnO films greater than 0.5 cm × 0.5 cm in size, the slide was tilted at 30° as shown in Figure 3.24 and the solution was added gradually. This approach allowed chromium outside of the initial etching solution to hold the gold in place and regularly provide new channels to allow the etching solution to access trapped regions of chromium when the ZnO or similar coating material forced the gold layer against the substrate to block existing pathways as shown in Figure 3.25. In this configuration, 40 mL of initial solution was used with 10 mL of additional solution added every 10 minutes to gradually expose the entire slide to the etching solution. If the gold film was not placed under tensile stress from the coating during the etching, drawing the gold film against the substrate to interrupt the channel, then the slide can be oriented vertically, fully immersed in the etching solution. It was also determined that increasing solution to temperature to 45°C would significantly increasing etching rate and tolerance for larger films as discussed below.

The total etching time was determined as the total time from when the potential was applied to when the chromium was visibly absent from the etching area. A completely etched slide produced using a tilted substrate and gradual addition of etching solution can be seen in Figure 3.26.

Handling of the slide and etching solution during the etching process also required significant care. Disturbances to the solution during and after etching could cause the gold to delaminate from the glass and float in the solution. Under extreme disturbances the gold would tear away completely. Once the etch was complete, as determined through a visible inspection of the backside of the substrate, the handling of the slide depended on the desired effect on the gold film and device. Drawing the glass slide through the etching solution may lift the gold film away from the surface of the glass. If the device on the gold film is stiff, removing the slide from the etching solution and shaking the gold film or substrate while the slide is still wet permits lifting or sliding the gold film and device from the glass slide. If the slide dries, the gold film lightly adheres to the glass surface, making removal difficult.

The effects of applied potential, temperature, ionic concentration, and stirring were all examined. Unless otherwise indicated, experiments were conducted at a reference potential of 0.8 V vs. Ag/AgCl, a solution temperature of 20°C, no stirring, and with an ionic concentration of 0.1 M, pH = 7 for sodium phosphate or pH = 10 for sodium hydroxide. These are referred
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Figure 3.25: Illustrations of a) how latent stress in the deposited film can cause the gold layer to deform against the glass, preventing etching solution access to the remaining chromium, and b) how increasing solution height creates new paths to etched trapped regions of chromium. Illustrations are not to scale.

to as normal conditions.

3.5.4 Results and Conclusions

3.5.4.1 Characterization of Blank Slides

Etching time as a function of etching distance for both phosphate and hydroxide solutions was measured and is shown in Figure [3.27]. Polyimide tape
3.5. Release of Films from the Substrate

Figure 3.26: Photo through the glass of a 1.0 cm×1.0 cm slide showing a fully chromium etched gold surface. The outline of the ZnO layer on the front of the slide can also be seen as reducing wrinkling in the gold layer.

was used to cover the long edges of the slides, only permitting etching along the 1.5 cm long base of the slide. Etching proceeded at the same rate along the full width of the slide, without favouring the centre of the slide over the edges. There is good agreement in etching rates between similarly prepared samples with hydroxide consistently taking longer than phosphate to etch. The slower etching rate may be the result of the lower molar concentration of hydroxide in the solution providing fewer ions to facilitate the charge transfer between the electrodes.

For uncovered slides (no ZnO or polyimide layer) the etching did not occur exclusively from the outside edge inward; regions of chromium etched concurrently throughout the entire slide. No holes or abrasions were found through SEM inspection of the gold surface. A slide was prepared with all edges covered to prevent etching from the edges of the slide inward. Etching performed using pH = 10 hydroxide under normal conditions indicated that etching still took place beginning at dozens of sites on the surface of the gold slide, indicating the presence of holes in the gold layer through which the etchant could reach the chromium. The access of the etchant to the chromium layer through such pinholes was obstructed through the deposition of an impermeable coating on top of the gold layer. A thicker gold layer might reduce the number of pinholes or prevent them entirely. For uncoated slides, the simultaneous etching of regions throughout the slide contributed to the error in measuring rate, particularly near the conclusion of the etching process.
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Figure 3.27: A plot showing mean etching distance as a function of time for solutions containing hydroxide or phosphate. The etching was performed on blank gold slides under normal conditions. Etching time was measured along one axis when the etching process crossed marked distance threshold on the slides. The horizontal error bars represent one standard deviation from the average, and vertical bars represent uncertainty in distance measurements due to the line widths of the markings on the slides.

The etching rate for a 5 nm thick layer of chromium and uncovered gold film is estimated at $2.4 \mu m/s$ for hydroxide and $5.5 \mu m/s$ for phosphate under normal conditions. These numbers represent the linear region near the beginning of the etching process as shown in Figure 3.27. Acceleration of the etching rate later in the process occurred consistently with every test as the area of chromium exposed to the etching solution rapidly decreased.

Voltammetry measurements were performed using a blank gold slide and are shown in Figure 3.28a. Current saturation was achieved between 0.5 V and 0.8 V with applied voltage vs. reference voltage, shown in Figure 3.28b, being linear in that range. Due to the wide operating range of the etching process, the experiment was also be conducted without a reference electrode by examining etching current and increasing it until the current is stable within 15% over a 0.2 V range.

The effect of applied potential was also examined by changing the potential to select a reference potential between 0.6 V and 1.0 V as shown in
3.5. Release of Films from the Substrate

Figure 3.28: Electrochemical voltammogram showing a) current vs. Ag/AgCl reference electrode for hydroxide and phosphate-based solutions, and b) Ag/AgCl reference electrode potential vs. total applied potential when sweeping the applied potential to produce a reference potential from 0 - 1 V at a rate of 1 mV/s. The samples under test were smaller Au/Cr/glass slides approximately 1.0 cm × 1.5 cm in dimension. The chromium was not completely removed from the sample by the end of this experiment.
Figure 3.29: A plot showing total etching time as a function of electrochemical reference potential for solutions containing hydroxide or phosphate. The etching was performed on blank gold slides under otherwise normal conditions. Error bars indicate uncertainty in determining completion of the etch.

Figure 3.29. The total etching time using hydroxide as the anion decreases linearly with increasing reference potential. From Figure 3.28 a non-linear response is expected between 0.6 V and 0.8 V although lower pH solutions reduce the magnitude of this non-linear effect, as shown. The phosphate etching time does not vary significantly despite the change in potential as expected from the relatively flat current response shown in Figure 3.28.

The anion concentration was varied to determine the influence of ion concentration on the total etching time with the results shown in Figure 3.30. Phosphate ion concentrations above 0.01 M yielded a slight increase in etching rate with increasing concentration, whereas below that threshold the etching rate decreased significantly. A similar behaviour was seen for hydroxide, where ionic concentrations above 0.1 mM increased the etching rate gradually and concentrations below caused a rapid drop in etching rate. Although hydroxide is a slower etchant, it remains consistently effective at lower solution concentrations than phosphate.

The pH of the phosphate and hydroxide solutions were measured before and after the etching was complete using pH strips and were found to be the
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![Graph showing etching time vs. concentration of anions](image)

Figure 3.30: A plot showing total etching time as a function of etching solution concentration for solutions containing hydroxide or phosphate. The etching was performed on blank gold slides under otherwise normal conditions. Error bars indicate uncertainty in determining completion of the etch.

same within measurement error, although a drop of 0.5 in hydroxide pH was observed at pH > 10, indicating that some hydroxide is chemically consumed in either the etching process or by reacting with the copper counter electrode.

The effect of solution temperature is shown in Figure 3.31. Etching rate is similar within error for both solutions from 65°C to 85°C with 45°C providing the fastest etching time for both ionic solutions. Operating at 85°C required refilling the solution with distilled water periodically to compensate for evaporation and ensure a consistent etchant concentration. It is not clear why 45°C presented a local maximum in etching rate.

The effect of stirring was also examined by adding a 1 cm long, 2 mm wide magnetic stir rod to the center of the dish and rotating the stir rod at 300 RPM throughout the etching process. Etching times of experiments using hydroxide conducted under normal conditions reduced from 25 minutes on average to 10 minutes. Similar experiments involving phosphate resulted in etching times of 6 minutes rather than the 9 minutes required to complete the etch without stirring. Stirring did have a negative consequence in that the freed gold film was torn away from the substrate in approximately half
3.5. Release of Films from the Substrate

Figure 3.31: Total etching time as a function of solution temperature for solutions containing hydroxide or phosphate. The etching was performed on blank gold slides under otherwise normal conditions. Error bars indicate uncertainty in determining completion of the etch.

3.5.4.2 Etching and Characterization of Coated Slides

Etching experiments were performed using both polyimide and ZnO coated slides. Dimensions of coating materials were varied, but the coating materials were always situated in the center of the test slide. The ZnO layer was electrochemically deposited and varied between 40\(\mu\)m and 50\(\mu\)m in thickness. The 76\(\mu\)m thick polyimide had an adhesive backing and was physically applied to the gold surface. The surface coatings prevented the etching solution from reaching the chromium layers except by travelling between the glass and gold layers. They also applied stress to the gold layer, potentially impeding the etching process by pinching the gold against the glass and preventing etching solution from reaching chromium beneath the coating layer. The etching times are summarized in Table 3.1. In all cases, coated slides did etch more slowly than uncoated slides. The etching rate for the polyimide coated slides was consistent between experiments and did not change significantly with coating size. Etching ZnO samples was less predictable,
3.5. Release of Films from the Substrate

Table 3.1: Etching Times for Coated Slides

<table>
<thead>
<tr>
<th>Material</th>
<th>Size (cm²)</th>
<th>Etchant</th>
<th>Total Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyimide</td>
<td>0.36</td>
<td>Phosphate</td>
<td>50 ± 15</td>
</tr>
<tr>
<td>Polyimide</td>
<td>1.0</td>
<td>Phosphate</td>
<td>58 ± 20</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.25</td>
<td>Phosphate</td>
<td>154 ± 50</td>
</tr>
<tr>
<td>ZnO</td>
<td>1.0</td>
<td>Hydroxide</td>
<td>420 ± 140</td>
</tr>
</tbody>
</table>

with some samples failing to completely etch free from the glass substrate. Tilting the substrate and gradually applying the solution as described in the Appendix A.2 helped significantly and was necessary for etching slides with ZnO coatings greater than 0.5 cm × 0.5 cm in size.

The etching distance profile of a partially covered slide is shown in Figure 3.32. A 1 cm wide strip of polyimide tape was adhered to the slide 2.5 mm from the edge in the direction of etching. Etching rates are similar for both the covered and uncovered films prior to encountering the obstruction. Once under the tape, etching slows significantly and proceeds with a similar profile as the hydroxide etch shown in Figure 3.27. The etching rate calculated early in the etching of the covered area is 2.2 µm/s compared to the etching rate of 9.1 µm/s of the uncovered section.

For slides coated with 1.0 cm × 1.0 cm of ZnO, it was not possible to complete an etch at room temperature without tilting the slide and adding etching solution gradually. The etching process would proceed only to terminate prematurely, presumably due to latent stress in the film forcing the underetched portion of the gold film against the glass and preventing the ionic solution from reaching the remaining chromium. Smaller dimension ZnO films of 0.5 cm × 0.5 cm were successfully etched to completion with every test.

No particulates were formed in any etching experiment. The impact of the hydroxide etching procedure on the surface morphology of the ZnO film is shown in Figure 3.33. There is no discernible difference in the morphology of the surface of the bare ZnO film after the etching process, suggesting that hydroxide is a good etching anion for removing the underlying chromium without impacting the structural and morphological properties of oxides like ZnO.

Unlike using hydroxide as the anion, a distinct effect on the surface morphology of the ZnO film is apparent when etching with phosphate as shown in Figure 3.34. Figure 3.34a compares the bulk of the etched film to
3.5. Release of Films from the Substrate

Figure 3.32: Shown are etching times as a function of distance of 1) a sample with only glass/Au/Cr etched in phosphate under normal conditions, 2) a sample covered with a 1 cm wide strip of polyimide tape beginning 2.5 mm from the edge etched in phosphate under normal conditions, and 3) a sample covered with a 1 cm² ZnO layer beginning 4 mm from the edge etched vertically in hydroxide (did not complete) under normal conditions. Time was measured as the etching process crossed marked distances on the slides.

that of the pristine, unetched ZnO film shown in Figure 3.34b. The bulk morphology remains very similar, indicating that the damage imposed by the phosphate etching is limited to the surface of the film. The etched film is also visibly discoloured, further indicating a change in its composition.

3.5.4.3 Summary of Slide Release

The electrochemical etching of nanoscale-thickness chromium adhesion layers to lift off gold layers and a deposited structure using an electrochemical method was demonstrated. Total etching time as a function of applied potential, anion concentration, temperature, and solution agitation was explored. The effect of coating the gold surface was also examined for varying sizes of polyimide and ZnO coating layers. Using hydroxide as the reaction anion resulted in a basic solution but facilitated a fast etch and release.
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Figure 3.33: SEM images taken at 20 kV showing a ZnO film grown at 3 mA/cm² current density a) before and b) after etching the chromium layer in pH = 11 sodium hydroxide.

of gold and ZnO film without damaging the ZnO structure. A similar etch using phosphate as the anion was also examined due to its potential applications in biological and pH-sensitive MEMS devices. The phosphate etching process was faster than using hydroxide but it did modify the surface of the ZnO film, indicating poor chemical compatibility with oxides. Other anions such as nitrates and chlorides were tested and showed poor selectivity, etching the gold as well as the chromium.
Figure 3.34: SEM images taken at 20 kV showing the effect of a 90 minute sodium phosphate etch on the surface morphology of ZnO where a) is the edge of the film exposed after etching and taken at 45° to the horizontal and b) is a similar image of a pristine, unetched ZnO film. The effect appears confined to the surface and does not change the morphology of the bulk.

3.6 ZnO Nanostructural Growth

ZnO-based nanostructures are defined here as materials based on ZnO that possess features, such as dimensional constraints (ie. nanowires), interfaces (ie. sintered nanoparticles), or structural variations (ie. nanovoids, heterostructures) with dimensions under 1 µm in size. ZnO can be formed into nanowires, stacked platelets, thin films, nanotrees, nanotubes, and other complex structures[40]. In Section 2.2 various nanostructures were theoretically considered for their relative thermoelectric potential. Although these
structures cannot be electrochemically synthesized using the methods proposed herein, attempts were made to demonstrate proof of concept formation of nanostructures at a larger scale. Of the structures considered, template assisted nanowires, nanovoided bulk films, and heterostructures were explored experimentally. Of these structures, only the nanovoided bulk films were fully synthesized and characterized. Experimental details and the results on the growth of the other structures can be found in Appendix A.4.

3.6.1 Nanovoided Bulk Growth

Nanovoided bulk materials are bulk materials that have a high density of localized lattice defects (voids) that scatter phonons, thereby reducing thermal conductivity. The modelling study described in Chapter 2 suggested that a nanovoided bulk ZnO configuration may be the best performing thermoelectric configuration possible of the nanostructured variations studied. Nanovoided materials have been successfully fabricated through a variety of processes with some of the best examples coming from ball mill and sintered Al:ZnO\[62, 69, 85, 179–182\]. Methods such as ball mill and sintering are limited in their ability to generate anisotropic features such as gradient doping patterns, so the focus in this section is the formation of nanovoided structures grown using an electrochemical method and sacrificial material.

3.6.1.1 Zinc Hydroxide Method

As observed in Section 3.4, the electrochemical formation of Al:ZnO does not generate a pure crystal. Some particles of Zn(OH)$_2$ persist within the film, interfering with crystal growth and film conductivity. This effect was also witnessed by others, who demonstrated that a subsequent low temperature (<400$^\circ$C) annealing step thermally decomposed the remaining hydroxide, leaving multiple submicron-sized pockets within the film\[156\]. Using a similar procedure, a reaction was noted in this work when Al:ZnO films were annealed at low temperatures, with films turning from transparent to opaquely white while concurrently deforming along all axes. The low temperature anneal was also accompanied with a improvement in film electrical conductivity when measured independently.

To better understand the behaviour of the intermediate Zn(OH)$_2$ step, separate solutions of 0.1 M Zn(NO$_3$)$_2$ and 1 M NaOH were prepared. At room temperature, 100$\mu$L drops of NaOH were added to the solution of zinc nitrate. Every drop generated a sudden burst of nearly transparent, fine, white precipitate that appeared in solution and sunk to the bottom.
of the beaker without aggregating. The material retained structure and translucency such that subsequent drops of sodium hydroxide quickly filled the beaker with a hazy, white suspension giving the beaker a cloudy look without forming a solid structure. Straining the solution through a filter and then analyzing the resulting white powder with an SEM produced images shown in Figure 3.35.

The white powder consisted of nanoparticles of Zn(OH)$_2$ measurably ranging from 10 nm to 300 nm in size. Although the conditions in an electrochemical bath are not identical to those in this experiment, the tendency for Zn(NO$_3$)$_2$ to form nanoparticles when exposed to small quantities of ba-
sic hydroxide may inform the formation of pockets of zinc hydroxide within the film. To confirm the presence of these particles, conventional 1 mA/cm² films were galvanostatically grown under the conditions described in Section 3.2 and Section 3.3.1. The films were annealed at 200°C and the resulting white film was mechanically broken in half. The cross-section of the film was examined using an SEM as shown in Figure 3.36, indicating the presence of varying densities of voids throughout the film. The void sizes are also consistent with the Zn(OH)$_2$ particles shown in Figure 3.35.

Figure 3.36: SEM images taken at 15 kV showing 200°C annealed, undoped ZnO where a) shows the cross-section of the film, b) shows a higher zoom section of the cross-section covered in small voids, c) shows another section of the film also covered in holes, and d) magnifies the voids themselves which range from 50 nm to 400 nm in diameter.

The integration of voids into the film by performing a low temperature anneal of the film was successfully demonstrated, although more work to better control the size and distribution of the voids is recommended.
3.7 Growth and Release Summary

3.6.1.2 Eosin Y Dye Method

Eosin Y is a common red/yellow organic dye. When used during electrochemical deposition of ZnO, the dye integrates into the film and can then be dissolved after the deposition is complete, leaving pores within the ZnO film[85]. Experiments have been successfully completed using both nitrate and chloride ZnO growth systems[179, 180, 183, 184]. Once film growth is complete, applying a diluted base solution dissolves the dye, leaving voids and a highly porous ZnO film[85].

Undoped films were grown using the conditions described in Section 3.2 and Section 3.3.1 with the addition of 50µmol/L Eosin Y to the grown solution at the beginning of the deposition. The dye adsorbed very effectively into the film, producing a bright red colouring once the deposition was complete. The red film was then immersed in 100 mL of pH = 12 KOH solution for 12 hours to remove the dye. Despite the long duration, there was no detectable change in the colour in the film. Desorption experiments performed by others used very thin films of ZnO, with some authors noting that even with thin films the dye did not completely desorb[183]. The red film after desorption was placed in the SEM to examine its morphology, but although small voids were seen on the surface of the film, they did not permeate throughout the film.

Although the use of the dye as a sacrificial material is well established in literature, the ability to remove the dye from thicker ZnO films is very limited due to the inability of deeply integrated dye to desorb through exposure to potassium hydroxide.

3.7 Growth and Release Summary

ZnO was successfully synthesized using an electrochemical method. A significant challenge was improving the existing ZnO electrodeposition methodology to enable the growth of thicker, high quality films. Existing methodologies involved counter electrodes that resulted in a drop in solution pH during the growth period, causing damage to the grown films. Potentiostatic growth with an Ag/AgCl reference electrode also proved inappropriate for thicker film growth due to the buildup of contaminant chemicals within the film as the growth proceeded. The contaminants caused morphological, crystalline, and electrical effects all detrimental for a ZnO-based thermoelectric material. Al:ZnO was successfully synthesized with aluminum integration above 2% demonstrated, a ratio that others have determined provides the best thermoelectric performance in the material system[44, 53]. One significant
3.7. Growth and Release Summary

The challenge to overcome is in improving the conductivity of the film. Although the films show extremely good growth selectivity along $\langle 002 \rangle$, the electrical conductance of the film is much lower than expected, likely attributable to Zn(OH)$_2$ nanoparticles that are integrated into film during deposition interfering with the monocrystallinity of the film. The activation of the aluminum within the film is also poor, but can be improved through low temperature annealing.

Al:ZnO films up to $45 \pm 5 \mu m$ in thickness were successfully synthesized using a low cost, scalable fabrication technology. Conventional methods for gaining access to both sides of the ZnO film were explored but were found not suitable. A methodology was developed for separating the films from the glass growth substrate by using electrochemical chromium etching, enabling access to both sides of the films without the risk of mechanically freeing the film or affecting the chemical and morphological integrity of the samples.

Nanostructured films were also successfully grown, although feature sizes within the films were 1-2 orders of magnitude larger than those examined through modelling work in Chapter 2. Template-assisted nanowire arrays and ZnO/Zn heterostructure films were synthesized, but were not pursued further due to fabrication challenges involving their consistency, quality, and fragility (see Appendix A.4). Voided nanostructures were fabricated using two methods: Dye integration and low temperature annealing. The former was able to produce small voids across the surface of the ZnO film but the dye removal process was unable to penetrate the full thickness of the film. The latter worked well, producing voids throughout the bulk of the film with diameters ranging from tens of nanometres to hundreds of nanometres. The annealing of the films caused the films to warp and change shape, which must be considered when characterizing the films in a thermoelectric test apparatus.

The voids in the ZnO films were larger than those modelled in Section 2.2.9 and their consistency within the bulk material was qualitatively less than the 30% volumetric voiding proposed in that section. Voids in the experimentally grown films should reduce film thermal conductivity to a lesser extent than those examined in the modelling work, but may still have a favourable STEF due to the reduced effect on electrical conductivity. Phonons with long MFP will still be disrupted where electrons, which generally have much shorter MFP, will propagate unhindered by the voids. The integration of hydroxide and poor crystallinity will be the dominant factors affecting both electrical and thermal conductivity. For greater modelling accuracy, future work could increase simulation cell size to optimize the void size and density at larger scales to allow comparison with experi-
mental results. Growth parameters affecting the void size and density, such as solution pH and nanoparticle preloading, could also be explored. More immediate challenges to overcome are the poor dopant activation of the aluminum and overall low electrical conductivity of the doped films.
Chapter 4

Thermoelectric Characterization of ZnO Films

Full characterization of a thermoelectric material involves determining critical material parameters over a range of temperatures such as the Seebeck coefficient, electrical and thermal conductivities, thermal expansion coefficients, and melting temperature. The former three parameters are the most critical for determining the thermoelectric performance of a material as described by (1.11) and (1.19). Characterization of thermoelectric materials is commonly performed using either direct measurement or Harman measurement[185–187]. Direct measurement involves placing a material sample between two electrodes and applying a known thermal flux through the material. The temperature on either side of the material is measured, along with its electrical conductivity and Seebeck-induced voltage. The material is tested at multiple temperatures to determine the temperature-dependent Seebeck coefficient and conductivity trends.

The Harman method involves situating a material in an adiabatic environment and applying a current through the material. The applied current generates a Peltier cooling response across the material which produces a temperature gradient. The current is then stopped and the potential across the material is immediately measured, which, when combined with an alternating current (AC) potential measurement to yield film electrical resistance, can be used to calculate $ZT$ directly[186],

$$ZT = \frac{V_{dc}}{V_{ac}} - 1.$$  \hspace{1cm} (4.1)

Enhanced versions of the Harman method also exist, incorporating temperature measurements to yield specific material properties[187], or transient excitation for greater accuracy in measurements[188]. Like the direct method, the Harman method is best applied to thick thermoelectric materials where thermal conductance is lower and interface uncertainties can be
minimized. The Harman method also requires that the material have sufficient thermoelectric performance to produce a useful temperature difference across the material that won’t immediately dissipate back through the film.

Despite its growing popularity, the Harman method may provide large errors when characterizing thin film materials due to the non-negligible effects of contact resistance and heat leakage\[189\]. Direct measurement is the preferred method for characterizing anisotropic, low dimensional, thermoelectric materials, although its use also presents challenges\[190-193\]. Thermal losses and ambiguity in interface effects between the test apparatus and device under test (DUT) often limit accurate thermoelectric characterization to only the material Seebeck coefficient\[191-193\].

To minimize interface errors, direct and Harman methods for characterizing thin film thermoelectric materials are typically performed by applying heating and characterization electrodes directly on to a material through cleanroom techniques such as metal evaporation\[188, 194, 195\]. New modelling and characterization methods are also continuously under development to allow more accurate characterization of microscale material samples and modules\[124, 130, 196-199\]. A significant limitation in these methods when deployed experimentally is that integrating the thermoelectric test apparatus onto the film or module requires that the apparatus be reconstructed with every film tested. Calibration and independent verification of performance are also difficult as each apparatus can only test a single sample.

Characterizing the effect of the interface between the thermoelectric material and the test apparatus is another challenge in thin film thermoelectric characterization. Due to the small volume of material under consideration, the interface between that material and the surrounding apparatus can play an important role in electrical and thermal characterization of the device. Malleable interface materials with exceptionally high thermal and electrical conductivities are desired which can mount flush against the surface of the test material while also permitting the direct application of a known thermal flux and temperature gradient to the material.

Many material properties, including electrical resistance, crystallinity, and surface morphology, have already been investigated in Chapter 3. A variety of thermal interface materials are tested for their potential use in thermoelectric direct measurement, and a custom, reusable thermoelectric test apparatus is constructed, calibrated, validated, and used for the characterization of thin films.
4.1 Interface Materials

An interface material forms the interconnect between the thermoelectric material, Al:ZnO, and the surrounding module or test apparatus. The material must provide an ohmic contact with very high thermal and electrical conductivities, deform to fill vacancies between the apparatus electrode and test material surface, and be deployable in extremely thin layers to minimize its influence on the characterization of the thermoelectric material. Five materials were examined for their viability, including GaInSn liquid metal eutectic from GalliumSource, LLC, Carbon Conductive Grease from MG Chemicals, CW7100 Silver Conductive Grease from Chemtronics, High Conductivity Silver Paint from SPI Supplies, and Wire Glue from Anders Products. GaInSn and other gallium-based liquid metals have been used in thermoelectric characterization for over 50 years[200], whereas the other materials selected are newer and are designed for heat sinking or high conductivity adhesion applications.

4.1.1 Material Electrical Characterization

Table 4.1 details the results of electrical resistance measurements. First, a template was used to shape the potential interface material into a 3 mm long by 1 mm wide strip on glass. Stainless steel needle probes were placed on opposite ends of each strip to act as electrodes. Current-Voltage (IV) curves were taken using a Keithley 2635A Source Meter by sweeping the voltage from $-2 \text{ V}$ to $2 \text{ V}$ at 0.02 V steps taken every 5 seconds. At least three data sets were collected for each experiment and median values are shown. The Drop on Gold experiments involved placing a $3.0 \pm 0.5 \text{ mm}$ droplet of the material directly onto a gold coated, glass slide and measuring the conductance from a steel needle probe through the material to the gold substrate. The Drop on ZnO experiments were identical to the Drop on Gold experiments except that the droplet of interface material was placed on identical, 45 µm thick films of ZnO grown on gold using the procedures described in Section 3.4. The ZnO was still located on the original gold growth substrate for the drop test.

Materials demonstrating an ohmic contact presented a constant slope between the indicated voltages. Materials demonstrating a Schottky contact were non-linear, showing exponential growth in current with increasing voltage, decreasing voltage, or both. Of all the materials characterized, only GaInSn was deemed electrically suitable for interfacing directly to ZnO.
4.1. Interface Materials

Table 4.1: Summary of IV test results for characterizing the measured resistance, $R$, and IV curve shape of different interface pastes, glues, liquids, and greases. Values should only be considered accurate within an order of magnitude and are intended for the comparison of different possible interface materials rather than providing data on the absolute electrical performance of the tested materials. Contact area between the material and substrate was regulated to $5 \pm 2\, \text{mm}^2$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Droplet</th>
<th>Drop on Gold</th>
<th>Drop on ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R(\Omega)$</td>
<td>Shape</td>
<td>$R(\Omega)$</td>
</tr>
<tr>
<td>GaInSn</td>
<td>0</td>
<td>Ohmic</td>
<td>1000</td>
</tr>
<tr>
<td>Carbon Grease</td>
<td>1000000</td>
<td>Ohmic</td>
<td>300</td>
</tr>
<tr>
<td>Silver Grease</td>
<td>100</td>
<td>Ohmic</td>
<td>0</td>
</tr>
<tr>
<td>Silver Paint</td>
<td>10</td>
<td>Schottky</td>
<td>2</td>
</tr>
<tr>
<td>Carbon Wire Glue</td>
<td>3000000</td>
<td>Ohmic</td>
<td>300</td>
</tr>
</tbody>
</table>

4.1.2 Interfacing to ZnO Films

SEM images of grown ZnO films, shown in Figure [4.1], were taken to determine the roughness of the interface on both sides of the film. Undoped ZnO films were grown using the parameters discussed in Section 3.4. The films were grown to a thickness of approximately $95 \pm 5\, \mu\text{m}$ as measured by SEM, and chromium etching was used to remove the films from the glass substrate as described in Section 3.5. The gold film on the underside of the ZnO was also gently removed using tweezers, exposing both sides of the film. As shown in Figure [4.1a and 4.1b], the underside of the ZnO has excellent coverage on the gold substrate and is acceptably flat with average roughness under $200\, \text{nm}$. The side exposed to the solution where growth occurs is significantly rougher, with roughened blades of ZnO extending up to $5\, \mu\text{m}$ from the surface of the ZnO. GaInSn, a yield stress fluid, demonstrated high viscosity and malleability when tested with probe tips, suitable for contacting a rough surface.

A method for applying a thin layer of GaInSn over contact materials was developed. Placing a drop of the material onto any substrate, including glass, polyimide, and metals such as copper and steel, then using the syringe to recover the majority of the GaInSn, left a microscale layer of the liquid.
4.1. Interface Materials

Figure 4.1: SEM images taken 20 kV at 45° angles showing a) gold side ZnO film surface and cross-section, b) gold side ZnO film surface (close up), c) solution side ZnO film surface and cross-section, and d) solution side ZnO film surface (close up).

metal lightly adhered to the substrate. The thin layer could then be spread across the surface of the substrate using a conventional Kimberly Clark Kim Wipe. Once the surface of the substrate was coated with a thin layer of liquid metal, more GaInSn could be added using a syringe. The additional material would wet extremely well across the entire substrate, forming a visibly flat and reflective layer of liquid metal that could serve as an interface between two stiff, porous surfaces. Although this method was not attempted on ZnO due to the fragility of the film, it was successfully deployed on both steel and graphite surfaces, which were then used as physical electrode materials for the thermoelectric test apparatus. The transparency of the ZnO films enabled verification of a good contact by observing the spreading of GaInSn on the underside of films as they were pressed against GaInSncoated apparatus electrodes.

Although it is possible that gallium diffused into the ZnO films during
testing, there was no evidence of changes in film electrical or thermal properties over multiple days of testing. The expectation is that gallium would either replace zinc or aluminum within the film lattice, effectively doping the films. This behaviour would correspond to an increase in thermal and electrical conductivity, which was not apparent throughout testing.

4.2 Themoelectric Tester

As the general thermal properties of the electrochemically grown ZnO films were unknown, and given the high electrical resistivity of the films tested in Section 3.4, the Harman method could not be chosen as an initial test methodology. Testing materials with high thermal conductivity and electrical resistivity cause measurement errors due to resistive heating, and rapidly dissipate the Peltier-induced temperature gradient, requiring extremely high resolution instruments to measure the Seebeck coefficient. The direct method was therefore chosen to measure the thermoelectric properties of the films. The direct measurement of the thermoelectric properties of thin films occurs almost exclusively using heater and sensor elements applied directly to the thin films using clean room techniques, as large, reusable apparatuses often have difficulty in distinguishing between interface materials and the DUT\cite{194, 195, 201}. Despite this challenge, with ZnO films in excess of 40\(\mu\)m in thickness realized through electrochemical growth, and given the high electrical resistivity of the film, a low cost, two electrode, reusable direct method apparatus was constructed to perform thermoelectric measurements of the grown films.

4.2.1 Design

The design of the apparatus was separated into two components: The enclosure and the heater probe. Each component was designed to be fabricated using low cost processes and materials while concurrently facilitating measurements of thin films down to 50\(\mu\)m in thickness and 1 cm\(^2\) in cross-sectional area. Support for temperature gradients from room temperature to 450\(^\circ\)C at the heater probe was also considered essential. Early FEA simulations and experiments using a simple resistive heater and doped silicon pieces of various dimensions confirmed that open air thermoelectric measurements were too inaccurate and impractical regardless of the complexity of the calibration process, and a design capable of performing measurements in a vacuum was deemed essential. A maximum applied thermal power of
20 W was chosen for the design, allowing for the use of forced air cooling of the apparatus heat sink.

Electrical resistivity and the Seebeck coefficient were measured using an Agilent 2635A System Sourcemeter. Power for the electrical heater element was provided by an Agilent N5751A DC power supply. Temperature measurement was performed using Maxim MAX31855 K-type cold junction temperature compensated thermocouple interface ICs connected to a Netburner kit for SPI to Ethernet conversion. The vacuum was provided by a Vacuubrand RZ-6 rotary vane pump and was measured to be below 0.01 mBar for all experiments. LabView was selected as the software package to interface with measurement equipment and perform automated temperature steps and measurements. Both Netburner and Labview code can be found in Appendix B and Appendix C respectively.

4.2.1.1 Test Apparatus Enclosure

The test apparatus enclosure consisted of a polished, 1/4" thick aluminum plate drilled with holes for wire feedthroughs. A drawing for the plate can be found in Appendix B. A groove was cut in the plate to allow the enclosure lid to sink into the rubber gasket and form a seal. Bolts in each corner of the enclosure outside of the vacuum area provided mounting for support posts which raised the apparatus high enough to allow the adhesion of a heat sink and fan to the underside of the base plate directly beneath the location of the device under test. Figure 4.2 illustrates the configuration of the test apparatus enclosure. Wire feedthroughs were populated with brass pins soldered to wire and then potted in place using two part resin epoxy.

Thermocouple interface electronics were located within the vacuum area of the enclosure to minimize potential sources for noise and interference on thermocouple leads. The thermocouples used were Omega CHAL-005 K-type base wire thermocouples with 12” lengths and 0.005” diameters. The small diameter was selected to minimize conductive heat losses through the thermocouple leads. The entire apparatus was covered during operation using a hemispherical aluminum bowl resting on a 1/8” neoprene rubber gasket. Both metal and glass covers were considered, but metal produced a more reliable seal at low cost, and its opaqueness and high thermal conductivity facilitated a more consistent radiative power transfer calculation as discussed in Section 4.3.1. An opaque cover also prevented optical excitation of oxygen dopants in the ZnO films[202].

To apply a consistent force on the heater probe and DUT, a pivot armature was constructed. A T-shaped steel and glass rod assembly connected
loosely to an inverted steel bolt rested on the heater probe during testing as shown in Fig. 4.2. Weights placed on the opposite end of the horizontal steel rod allowed for the configuration of the applied force to the heater probe located at the base of the vertical glass rod component of the assembly. The 1 mm thin, 7.5 cm glass piece provided good thermal resistance while also supplying sufficient mechanical stiffness to hold the heater probe in place. A design involving a strain gauge and two bolts on either side of the rod assembly was also constructed and tested, but even slight flexure in the aluminum base plate while transitioning to and from the vacuum state caused radical shifts in the force applied to the DUT. A free weight system compensates for slight mechanical deformations of the base plate, permitting the use of a thinner material and correspondingly improved heat dissipation. The entire rod assembly weighed 48 g and 36 g of additional weight was added at the far end of the 9.2 cm long pivot, yielding a downward force of 1.2 N onto the probe. Attempts at providing a greater force typically resulted in the fracture of the ZnO films.

4.2.1.2 Test Apparatus Heater Probe

The heater probe provided several functions. It converted applied electrical current to thermal power, measured temperature as close to the top of the DUT as possible, conveyed a uniform force across the surface of the film, provided a uniform and low resistance electrical contact across the surface of the DUT, and withstood high temperatures in a vacuum environment.
without significantly changing its electrical, thermal, or optical characteristics. On the underside of the DUT, the base plate performed complementary functions, including sinking thermal energy, measuring temperature as close as possible to the bottom of the DUT, providing a low electrical resistance contact, and evenly contacting the entire bottom surface of the DUT. One of the greatest challenges in measuring thin films using this direct method was in avoiding a short circuit between the heater probe and base plate.

An illustration of the heater probe and base plate assembly is shown in Figure 4.3. The heater probe was designed using a conventional bottle cap as a substrate. The thin steel, once sanded and polished, provided an acceptably flat and conductive surface. The ridges around the cap also provided crimping sites for connecting a 26 AWG electrical wire to the heater probe without the need for solder, thereby simplifying interconnectivity at high temperature and allowing easy and low cost replacement of the heating element. The 26 mm outer diameter, 5.5 mm high cap was filled with a 3 mm thick layer of Omega OB-400 thermally conductive cement. Approximately 30 cm of Manelco NW60-36 AWG nichrome (nickel chromium alloy) wire was coiled and then placed in a circular formation into the cap. Earlier experiments with pre-wound tungsten coils failed to reach temperatures of 350°C without failure, as the tungsten oxidized due to contact with the cement and fractured from thermal stress. The nichrome wire survived above 450°C and demonstrated negligible drift in resistance over the full temperature range. A thermocouple was then placed in the centre of the cap while the cement cured. The cement acted as a good electrical insulator, and despite the proximity between the nichrome, thermocouple, and steel of the cap, negligible electrical leakage current was detected. Both the nichrome coil and thermocouple were placed as low as possible into the cement to minimize the amount of material between the steel cap, thermal power source, and thermocouples.

Once cured over 24 hours, the cap was heated to 350°C for 12 hours to further cure the cement, at which point it turned a beige/rose colour. High current leads were connected to the nichrome element by twisting the wire ends together and thermocouple leads were directly soldered to their respective instrumentation ICs, leaving at minimum 15 cm of open wire to maximize thermal resistance. Similarly, a minimum of 15 cm in all other wire leads connecting to the heater probe was used to minimize conductive losses through the wiring assembly. Once in place, a thin GaInSn layer was applied to the underside of the heater probe in the approximate shape of the DUT. Experimentally, the DUTs tested strongly adhered to the heater probe through a vacuum suction effect resulting from a combination of the
4.2. *Thermoelectric Tester*

**Figure 4.3:** Close up diagram of the thermoelectric test apparatus heating element, interface, and DUT.

Liquid metal interface material and smooth surfaces of the DUT and probe. Excess GaInSn could then be removed from around the DUT to minimize the likelihood of a short circuit between the heater probe and the base plate.

Due to the strong chemical interaction between gallium and aluminum, a secondary material to cover the base plate and form the thermal and electrical contact with the DUT was selected. A thin graphite sheet (Panasonic EYGS091203), 3 cm long and 2 cm wide was selected for this purpose. The graphite sheet datasheet reported a thickness of 25μm with an in-plane thermal conductivity of $1600 \text{ W m}^{-1} \text{ K}^{-1}$ and electrical conductivity of $20,000 \text{ S/cm}$. The graphite was adhered to the aluminum plate using ITW Chemtronics CW7100 silver conductive grease. Adjacent to the 2 cm × 2 cm target area, a thermocouple was covered with polyimide tape and was placed on the graphite film. Measuring temperature directly beneath the DUT would have been challenging as the surface of the substrate must be extremely flat. The high thermal conductivity of the graphite was leveraged to minimize the temperature difference between the underside of the DUT and the thermocouple. The graphite was then covered with a thin layer of GaInSn using the same method and parameters for covering the heater probe.

Electrical measurements were performed using a 2-wire or 4-wire method. For large starting resistance above $25 \Omega$ a 2-wire method was used with resistance measured at 0.1 V applied across the film. For initial resistance below that threshold, both resistance and Seebeck voltage was measured using a 4-wire method with the signal wires connecting directly to the cap and graphite to minimize the effects of other losses in the system. Measured resistance of the 4-wire method under short circuit conditions was less than $15 \text{ mΩ}$ with $100 \mu\Omega$ resolution.
4.3 Thermoelectric Tester Calibration and Validation

4.3.1 Calibration Methodology

To maximize the accuracy of the measurements, a three step calibration process was devised. A simplified model of the heat transfer using electrical analogs is shown in Figure 4.4. $Q_H$ is the thermal power produced by the nichrome heating coil in the temperature probe. $T_H$ is the high temperature measured from the heater probe in close proximity to the surface of the DUT. $R_O$ represents the non-linear losses due to radiation, convection, and conduction from the heater probe to the surrounding environment. $R_H$ represents the linear thermal resistance between the high temperature thermocouple and the bottom of the heater probe as well as any resistive losses from the graphite on the base plate to its low temperature measurement thermocouple (represented by the ground in the figure). $R_I$ represents the total cross-sectional area dependent thermal resistance between the surface of the DUT and both the heater probe and graphite. $R_D$ is the thermal resistance of the DUT, which is what must be accurately measured.

![Circuit analog for heat flow through the heater probe, interface, and device.](image-url)

Figure 4.4: Circuit analog for heat flow through the heater probe, interface, and device.
4.3. Thermoelectric Tester Calibration and Validation

The first step in the calibration process is the open circuit measurement. For this measurement, no DUT is used and the heater probe assembly is suspended in the vacuum. Schematically, this represents the removal of $R_D$ and the direct measurement of $R_O$ by considering the difference between $T_H$ and ground ($T_L$) as a function of applied power. Ideally, the vacuum minimizes convective losses and proper cable management and thin wires minimize conductive losses. Both convective and conductive losses would present a linear relationship between power and temperature. Radiative losses follow the Stefan-Boltzmann law for power transfer,

$$Q_{\text{loss}}(T) = e\sigma A(T^4 - T_C^4),$$

where $e$ is the emissivity and $\sigma$ is the Stefan-Boltzmann constant. The equation represents a strictly fourth order relationship between power and temperature. Although an ideal instrument would only use the fourth order term, a full polynomial fit is performed over a wide range of temperatures and power settings to derive the open circuit relationship between heater probe temperature vs. enclosure temperature ($T_C$) and thermal power loss through methods other than the DUT.

The second step in the calibration process is the closed circuit measurement. This measurement involves coating a matching surface area of the heater probe and graphite base plate with GaInSn and then connecting the two together. This measurement sets $R_D$ to 0 and allows the determination of $R_H + R_I$. Electrical resistance and Seebeck coefficient are also measured as a function of temperature to provide a linear compensation factor for future DUT measurements. Ideally, this measurement would yield no temperature change as a function of heater power.

The third step requires the placement of a characterized, high conductivity material with a large Seebeck coefficient between the heater and the graphite. The purpose of this test is to determine the ratio between $R_H$ and $R_I$. This discrimination is important as the former is not dependent on the cross-sectional area of the DUT whereas the latter is. A proper ratio, with open and closed calibration data also considered, will yield concurrently correct thermal conductivity and Seebeck coefficients for the material under examination.

An additional correction involves measuring the resistance between the contacts on the heater probe to the source of the current for the heater. Knowing this resistance enables compensation for losses along the wiring to the heater. A continuous 4-wire measurement would be a better solution, but it was desirable to minimize the amount of wiring both within the dome and to the heater probe.
4.3. Thermoelectric Tester Calibration and Validation

The calibration as a whole is only strictly necessary when performing tests on materials with very high thermal conductivity or at high temperatures. Measuring the former is very sensitive to $R_H$ and $R_I$ whereas the latter is sensitive to $e$ and the accuracy of temperature measurements. Earlier experiments using a cooling coil located in the same vacuum chamber as the DUT and heater probe failed due to variations in temperature along the coil making predicting radiative transfer prohibitively complex.

The calibration coefficients are determined using the following steps:

- Load data sets from open and closed calibration runs.
- Subtract wiring resistive losses from the thermal power measurements of both losses, providing a corrected thermal power generated at the heater probe.
- Calculate a fourth order polynomial fit of open circuit differential temperature, $T_H - T_C$, vs. thermal power for $R_O$, normalized by full heater probe surface area.
- Calculate a first order fit of closed circuit differential temperature vs. thermal power for $R_H + R_I$, normalized by contact area between the probe and plate.
- Calculate first order fits for electrical resistance and Seebeck coefficients as a function of differential temperature.
- Load data from the high thermal conductivity sample.
- Apply open and closed circuit calibration coefficients (see below) iteratively while adjusting $R_{HI\text{ratio}}$ until measured thermal conductivity and Seebeck agree with material values.

These coefficients are then applied to data using the following steps:

- Load calibration coefficients and sample data set.
- Subtract wiring resistive losses from the thermal power measurements using measured cable resistance and current.
- Subtract thermal power due to radiative and conductive losses using $R_O$, after first adjusting the coefficients for the cross-sectional area of the DUT.
4.3. Thermoelectric Tester Calibration and Validation

- Recalculate $T_H$ using

$$T_{H\text{new}} = T_H - Q_H \left( R_{\text{adj}} R_{H\text{ratio}} + R_{\text{adj}} (1 - R_{H\text{ratio}}) \frac{A_{\text{closed}}}{A_{\text{DUT}}} \right) \quad (4.3)$$

where

$$R_{\text{adj}} = R_{H,\text{closed}} + R_{I,\text{closed}}, \quad (4.4)$$

$Q_H$ is the thermal power traveling from the heater element into the film, $R_{H\text{ratio}}$ is the ratio of thermal resistance of the heater element to the interface thermal resistance, $A_{\text{closed}}$ is the cross-sectional area of contact between the heater element and the base plate during closed calibration, and $A_{\text{DUT}}$ is the cross-sectional area of the device under test.

- Subtract closed circuit calibration resistance from the DUT electrical resistance measurement.

- Subtract closed circuit calibration Seebeck from the DUT Seebeck coefficient measurement then subtract a further 3 $\mu$V/K to adjust the value to reference platinum metal.

The following sections consistently use the above procedures for determining calibration coefficients and adjusting raw data collected from film samples.

4.3.2 Repeatability and Calibration

Once constructed, the apparatus was characterized using open and closed calibration methods and heavily doped n-type silicon as the high thermal conductivity material for the final calibration step. The calibrated system was used to characterize the thermoelectric performance of a variety of doped and undoped electrochemically grown ZnO samples to ascertain their value as thermoelectric materials. Seebeck coefficients listed in this section are referenced to platinum.

Experiments are performed by first positioning the heater probe, DUT, and armature assembly on the base plate. Electrical resistance measurements are checked throughout the procedure to ensure that no unexpected electrical short circuits are formed between the heater and the base plate. If the specified force of 1.3 N is successfully applied without an apparent short, the dome is placed onto the apparatus and the enclosed space is vacuumed to at least a moderate vacuum of 0.01 mBar. After thermal stabilization
4.3. Thermoelectric Tester Calibration and Validation

monitored using LabView, a small adjustment at room temperature is applied to compensate for any error in the thermocouples (typically 0.25°C to 0.5°C). A preprogrammed series of voltages are then applied to the temperature probe at 30 minute intervals first stepping up to a maximum thermal power output and then stepping back down. The process may be repeated within the same log to verify repeatability. An example of this sequence is shown in Figure 4.5.

![Figure 4.5: Probe and plate temperature as a function of time for two measurements of a ZnO film (see Section 4.4).](image)

Data points for detailed analysis are selected by hand by examining the plateaus at each power (or voltage) setting. Once a point on a plateau is selected, a mean average of 20 samples around that point is used in the following calculations, including calibration.

4.3.2.1 Calibration Measurements

Numerous open and closed calibrations were performed regularly to ensure consistency in device operation. Open calibrations may drift in time due to oxidation or discolouration of the heater probe changing its emissivity. Closed calibrations may vary due to changes in material properties, formation of oxide layers, and changes in surface roughness.
4.3. Thermoelectric Tester Calibration and Validation

The temperature vs. thermal power curves for a series of open calibrations are shown in Figure 4.6. Measurements were taken 5 weeks apart yet still showed excellent consistency despite heavy usage of the test apparatus. The non-linear fit shown in the figure represents a strictly fourth order fit using (4.2). The close fit indicates that the predominant mechanism of heat loss during open calibration is radiation, with conduction through wires playing only a very small role. Using the measured surface area of the heater probe, the calculated emissivity of the probe is 0.47. A fourth order polynomial fit including including lower order terms is indistinguishable from the experimental data on the plot and was used for compensating other data in this section.

![Figure 4.6: Induced temperature gradient between heater probe and base plate as a function of applied thermal power. The fit shown is a purely 4th order fit using (4.2). Three separate calibrations are shown.](image)

A similar plot for a closed calibration is shown in Figure 4.7. Unlike the open calibration, the resulting plots are linear and represent a much smaller change in temperature. If no thermal resistance was present between the thermocouples, the curves would be flat lines independent of power. The presence of the curves allowed the calculation of the total thermal resistance between the high temperature and low temperature thermocouples, approximately 0.36 K/W. Methods of reducing this thermal resistance, such as the
removal of the steel cap, were explored, but failed to yield an improvement in performance that offset the resulting detrimental effects such as increased fragility and the poor electrical isolation of components in the heater probe.

![Graph](image)

Figure 4.7: Temperature difference as a function of thermal power for a series of closed calibrations.

Figures 4.8 and 4.9 show the measured electrical conductance and induced voltage (related to the Seebeck coefficient) resulting from the closed calibration. Electrical conductance did not vary significantly as a function of temperature and remained within 10% between tests. Electrical conductivity compensation was only used for 2-point measurements. Induced voltage did change properties as the apparatus aged, possibly due to the formation of oxide or other material metallurgical changes affecting the Seebeck coefficient of the heater probe. The change indicates the development of an n-type Seebeck coefficient under closed calibration conditions. The initial Seebeck coefficient is $-1.5 \mu V/K$ and grows to $-10 \mu V/K$. A value of $-2.5 \mu V/K$ was chosen for compensating silicon and ZnO Seebeck measurements in the following sections.
4.3. Thermoelectric Tester Calibration and Validation

Figure 4.8: Electrical conductance as a function of average temperature for a series of closed calibrations.

Figure 4.9: Induced voltage as a function for temperature difference a series of closed calibrations.
4.3. Thermoelectric Tester Calibration and Validation

4.3.2.2 Silicon Measurements

To determine $R_{HIratio}$, a 500 µm thick piece of n-type silicon was used. The piece had a rated electrical resistivity of 0.001-0.005 Ω cm, indicating a doping concentration of between $1 \times 10^{19}$ and $1 \times 10^{20}$ cm$^{-3}$. A sample with a cross-sectional area of 0.75 cm$^2$ was cleaned with acetone and distilled water using ultrasonication for 5 mins. Figure 4.10 shows the temperature difference across the wafer as a function of thermal power before and after the calibration, including $R_{HIratio}$, was applied. The effect of calibration on the induced voltage can also be seen in Figure 4.11. $R_{HIratio}$ was selected to provide an optimally linear thermal conductivity and Seebeck coefficient close to the experimentally published values for doped silicon.

![Temperature as a function of thermal power before and after calibration of a 500 µm thick silicon wafer n-type doped to a resistivity of 0.002 Ω cm.](image)

For a $R_{HIratio}$ value of 0.63, the performance of the calibration can be seen in Table 4.2. The good agreement between thermal conductivity and Seebeck coefficient of the sample after calibration indicates that the calibration parameters and measurement methodology are suitable for measurements of films with thermal conductivity below approximately 10 W m$^{-1}$ K$^{-1}$. 
4.4 ZnO Thermoelectric Measurements

Figure 4.11: Induced voltage as a function of the temperature difference between the probe and the plate before and after calibration of a 500µm thick silicon wafer n-type doped to a resistivity of 0.002 Ωcm.

Table 4.2: Pre-calibration and post-calibration silicon wafer measurements.

<table>
<thead>
<tr>
<th>Measurand</th>
<th>Pre-Calibration</th>
<th>Calibrated</th>
<th>Reference [203]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity (W m$^{-1}$ K$^{-1}$)</td>
<td>7.44 ± 1</td>
<td>142 ± 10</td>
<td>140 ± 10</td>
</tr>
<tr>
<td>Seebeck Coefficient (µV K$^{-1}$)</td>
<td>−16.9 ± 5</td>
<td>−430 ± 20</td>
<td>−420 ± 20</td>
</tr>
</tbody>
</table>

4.4 ZnO Thermoelectric Measurements

ZnO films were grown in accordance with the procedures developed in Chapter 3. 1 cm × 1 cm ZnO films 45µm thick were grown and removed from their growth substrates using the chromium etching process described in Section 3.5 with hydroxide solution at pH = 11. When placed in the thermoelectric test apparatus, the films universally cracked or shorted. Thicker, larger films were grown to reduce the probability of the films fracturing, although some cracks were still detected in the films after testing. ZnO films 95 ± 5 µm
4.4 ZnO Thermoelectric Measurements

Thick were then grown without difficulty or visible change in film properties with thickness as verified by SEM measurements of the cross-section of the films. Films without doping were grown larger with cross-sectional areas varying from 1.2 cm$^2$ to 1.7 cm$^2$, measured using calipers. With the exception of longer depositions leading to thicker films, the growth methodology of doped films was identical to that developed in Section 3.4. A chemical target doping concentration of 4 µmol/L was used in all doped films to achieve an Al to Zn ratio close to 2%. The doped films were thinner than the pure ZnO films and were measured at 79 ± 5 µm in thickness using a SEM with the film tilted at 45°. The additional mechanical strength resulting from using thicker films enabled a significantly higher test yield.

4.4.1 Experimental Preparation

Samples were rinsed with distilled water and were dried in open air for 12 hours. After drying, they were inspected with a microscope where a fine needle was used to remove any remaining gold and break away sections of film with visible anomalies such as obstructions or discolouration. Sample dimensions were measured using calipers and area was calculated. The heater probe and graphite base plate were cleaned, polished, and coated with GaInSn before each sample was placed into the apparatus. The sample was placed onto the base plate, and the distribution of the GaInSn beneath the sample was visibly studied through the film to ensure good coverage. GaInSn was added or removed as required, with special care being necessary that no GaInSn beads escaped the circumference of the film. The heater element was placed onto the sample and weights were added to the assembly to achieve the desired force on the film. Electrical resistance measurements were then performed with voltages ranging from 0.1 V to 1.0 V to detect short circuits and ensure a linear response. The force on the heater probe was also perturbed by hand to determine the magnitude of response in the resistance and thus assess the reliability of the contact. Resistance was permitted to vary within 30% of its initial value. If any of these initial tests failed, the heater probe was removed, the apparatus was inspected, and the heater probe was returned for another attempt. Initial testing was repeated until the resistance was sufficiently stable to begin thermoelectric testing.

4.4.2 Annealing Process

Early experimentation revealed that testing newly grown films in the thermoelectric test apparatus would cause the films to anneal during the test in
4.4. ZnO Thermoelectric Measurements

a fashion consistent with observed results discussed in Section 3.4.2.4. At temperatures as low as 60°C, films would fail to maintain a temperature plateau during a continuous application of a non-varying thermal power. This behaviour would persist for several temperature steps in the test process until the film stabilized in a new configuration, which typically occurred after a prolonged (2 hour) anneal at the peak temperature of the test. A clear example of this behaviour is shown in Figure 4.12. Temperature is increased in regular increments until the 3.5 hour mark. Annealing is apparent beginning at the 1.5 hour mark and manifests as a sharp increase in thermal conductivity, although not all films were observed to behave in the same manner during annealing. The apparent dips in the plot correspond to the gradual increase in film thermal conductivity throughout the annealing process.

![Graph showing temperature differential across the film of a 3 mA/cm² current density ZnO sample showing ramp up and annealing as well as ramp down. Both ramp up and ramp down are programmed with the same thermal power step configuration and, without changes in film properties, should converge to identical temperature plateaus.](image)

Figure 4.12: Temperature differential across the film of a 3 mA/cm² current density ZnO sample showing ramp up and annealing as well as ramp down. Both ramp up and ramp down are programmed with the same thermal power step configuration and, without changes in film properties, should converge to identical temperature plateaus.

The annealing process occurs in both oxygenated and vacuum environments and affected all tested films. The annealing is likely the thermal decomposition of embedded hydroxide ions in the film, yielding ZnO and
4.4. ZnO Thermoelectric Measurements

AlO products and leaving vacancies such as nanoholes and microholes in the film as discussed in Section 3.6.1. Films deposited with higher current densities are more likely to integrate hydroxide ions into the film as less time is available during growth for the electrochemically evolved hydroxide ions to decompose into ZnO in the film.

All of the figures in this section represent nine sets of data collected from three samples of each indicated type of material. The power, rather than the applied temperature, was controlled throughout the measurement process, meaning that each sample converged to slightly different temperature plateaus depending on their material properties and dimensions. Samples could only be tested once prior to annealing. Data from films of the same type (i.e. 3 mA/cm\(^2\)) are indicated with the same colour and symbol. Three films of each material type are shown. Linear regression fits on the available data are used to show trending for each sample (dashed lines) and the overall average of all samples of a given type (thick, solid lines). Although sample behaviour is not expected to be purely linear over the temperature range considered, linear behaviour is a reasonable approximation.

Figure 4.13 shows the measured thermal conductivity as a function of average temperature of films sample grown at 1 mA/cm\(^2\), 3 mA/cm\(^2\), and 1 mA/cm\(^2\) with aluminum doping. A noteworthy observation is that the thermal conductivity of all films is orders of magnitude below bulk ZnO and Al:ZnO doped films fabricated using other methods\[32, 52, 53, 62, 153\]. A numerical comparison can be found at the end of this chapter. A flat or decreasing trend of thermal conductivity with temperature is expected and observed. The thermal conductivity of all samples measured was initially quite similar, with the exception of one Al:ZnO trial which produced a notably higher thermal conductivity prior to annealing.

The electrical conductivity and Seebeck coefficients of the films can be seen in Figures 4.14 and 4.16, respectively. The poor electrical conductivity of all grown films is consistent with observations made in Section 3.4.2.3 and is a significant hindrance in the thermoelectric performance of the films. The addition of the aluminum dopant does not have a significant effect on the electrical conductivity of the films, which is consistent with poor dopant activation. The high variability in the electrical conductivity results between different films is expected, as small variations in growth parameters can lead to significant variations in oxygen doping and electrical conductivity\[61, 204–208\].

The Seebeck coefficient is negative, indicating an n-type doped material as expected, but the Seebeck coefficient is a lower magnitude (−30 to −150\(\mu\)V/K) than commonly reported for the indicated level of doping.
4.4. ZnO Thermoelectric Measurements

Figure 4.13: Pre-annealed thermal conductivity as a function of average temperature for a variety of ZnO-based samples.

Figure 4.14: Pre-annealed electrical conductivity as a function of average temperature for a variety of ZnO-based samples.
4.4. ZnO Thermoelectric Measurements

Figure 4.15: Pre-annealed Seebeck coefficient vs. Pt as a function of average temperature for a variety of ZnO-based samples.

(−150 to −350 μV/K), although others have also reported lower magnitudes in doped samples[32, 52, 53, 62, 153]. As expected, the doped sample provides the lowest Seebeck coefficient. Unexpectedly, the 3 mA/cm² film demonstrates the highest Seebeck coefficient, suggesting that further research may benefit from focusing on higher current density deposition despite the rougher film surface and other limitations discussed in Section 3.4.

A flat or slight increase in Seebeck coefficient magnitude with temperature is also expected and is generally seen with ZnO and Al:ZnO up to 500°C[153].

The dimensionless figure of merit of pre-annealed films is shown in Figure 4.16. The gradual upward slope with temperature is expected as Al:ZnO and ZnO typically demonstrate their peak ZT at approximately 1000°C. The 3 mA/cm² current density films outperform the other samples, primarily due to having a superior Seebeck coefficient. The overall ZT of all the tested samples is too low for economic viability as a thermoelectric material in a pre-annealed state.

4.4.3 Performance of Annealed Films

Films were ramped up to a temperature exceeding 200°C and kept above that threshold for a period of 2 hours to allow any low temperature anneal-
4.4. ZnO Thermoelectric Measurements

Figure 4.16: Pre-annealed figure of merit as a function of average temperature for a variety of ZnO-based samples.

Annealing processes, such as hydroxide thermal decomposition, to complete. The stabilized films were then characterized using multiple temperature steps in a similar manner as in the previous section.

All of the figures in this section represent at least 25 sets of data collected from three samples of each indicated type of material. Data are represented identically to the previous section with the exception of the inclusion of error bars. Error bars represent the variation in a single sample’s measured properties over multiple tests, with a test representing either a ramp up or ramp down in temperature (room temperature to peak test temperature) with multiple plateaus.

The thermal conductivities of the annealed samples are shown in Figure 4.17. After annealing, the thermal conductivity of the undoped samples increased on average, with the thermal conductivity decreasing on average for the doped samples, suggesting that the improved activation of aluminum during the annealing process acts as a mechanism for improved phonon scattering. All films continue to present exceptionally low thermal conductivities.

Annealing did not significantly affect the electrical conductivity of the 3 mA/cm² sample. However, consistent with measurements taken in Sec-
4.4. ZnO Thermoelectric Measurements

The electrical conductivity of both the doped and undoped 1 mA/cm² samples increased significantly after annealing, exceeding the electrical conductivity of the annealed 3 mA/cm² sample. Electrical conductivity results are shown in Figure 4.18.

The Seebeck coefficients, shown in Figure 4.19 show an improvement for all samples, indicating either less internal electrical dissipation, lower dopant activation, or the additional formation of crystalline ZnO within the film. The concurrent improvements in Seebeck and electrical conductivity for the doped and undoped 1 mA/cm² samples indicate that a low temperature anneal, even under vacuum conditions, is beneficial to the thermoelectric performance of the material. Considering that the material is intended to operate at very high temperatures, this behaviour is a useful characteristic. The samples grown at 3 mA/cm² demonstrated a particularly favourable Seebeck coefficient, which is greater after annealing.

The final ZT of the samples can be seen in Figure 4.20. After annealing, the performance of the 1 mA/cm² film shows the greatest performance, although some samples of the Al:ZnO samples outperformed the 1 mA/cm² samples. Better activation of the aluminum within the samples with a corresponding improvement in electrical conductivity would lead to a much more...
4.4. ZnO Thermoelectric Measurements

Figure 4.18: Annealed electrical conductivity as a function of average temperature for a variety of ZnO-based samples.

Figure 4.19: Annealed Seebeck coefficient vs. Pt as a function of average temperature for a variety of ZnO-based samples.
4.5 Characterization Summary

pronounced improvement of the doped samples over the undoped samples. All samples benefited from the low temperature annealing process, with $ZT$ being an order of magnitude greater for the 1 mA/cm$^2$ samples after annealing.

![Figure 4.20: Annealed figure of merit as a function of average temperature for a variety of ZnO-based samples.](image)

4.5 Characterization Summary

Various thermally conductive interface materials were examined for their potential to enable the testing of thin films using a contact-based direct method of thermoelectric measurement. GaInSn was the only interface material tested with the properties necessary for use in thin film thermoelectric measurements. A method for coating a surface with a thin layer of GaInSn was developed and then deployed as part of the design and construction of a low cost thermoelectric apparatus suitable for measurements of ZnO-based thin films. The thermoelectric test apparatus was designed and constructed for under $1,000 CAD in materials, excluding the vacuum system and instrumentation, and was successfully calibrated using open, closed, and silicon sample configurations.

Samples representing high current density (3 mA/cm$^2$) ZnO deposition,
standard current density (1 mA/cm$^2$) ZnO deposition, and Al-doped standard current density (1 mA/cm$^2$) deposition were tested using the thermoelectric test apparatus to determine their properties prior to and after low temperature annealing. Film properties of these electrochemically grown films were compared to the room temperature performance of ZnO films produced by others using different methodologies in Table 4.3. Though the table represents some of the best known methods for developing thermoelectric Al:ZnO, the listed $ZT$ is lower than expected as room temperature performance is shown to ensure consistent comparison between materials. As illustrated in the table, there is great variability in the electrical and thermal properties of ZnO and Al:ZnO fabricated using different technologies, although no variations have produced thermal conductivities as low as those provided by the electrochemical method used herein. The electrical conductivities of the electrochemically grown ZnO films agree within an order of magnitude with thinner samples tested using the drop method described in Section 3.4.2.3 and are comparable to ZnO results published by others.$^{156, 204, 207, 209}$

The low electrical conductivity is a significant limitation in the material. It leads to a low $ZT$ when compared to measurements of films grown using alternative methods. If the electrical conductivity could be improved without proportionately increasing thermal conductivity, the resulting film would present significant promise as a thermoelectric material.
### 4.5. Characterization Summary

Table 4.3: A room temperature comparison of the thermoelectric properties of ZnO and Al:ZnO grown electrochemically (this work) and using other methods (other publications).

<table>
<thead>
<tr>
<th>Technology</th>
<th>$\kappa$ (W m$^{-1}$ K$^{-1}$)</th>
<th>$\sigma$ (S cm$^{-1}$)</th>
<th>$\alpha$ (µV K$^{-1}$)</th>
<th>$ZT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrochemical ZnO 1 mA/cm$^2$ Pre-Anneal</td>
<td>0.020</td>
<td>0.00023</td>
<td>-79</td>
<td>8.2e-7</td>
</tr>
<tr>
<td>Electrochemical ZnO 1 mA/cm$^2$ Post-Anneal</td>
<td>0.028</td>
<td>0.0022</td>
<td>-69</td>
<td>1.2e-5</td>
</tr>
<tr>
<td>Electrochemical ZnO 3 mA/cm$^2$ Pre-Anneal</td>
<td>0.023</td>
<td>0.00031</td>
<td>-96</td>
<td>4.2e-6</td>
</tr>
<tr>
<td>Electrochemical ZnO 3 mA/cm$^2$ Post-Anneal</td>
<td>0.037</td>
<td>0.00041</td>
<td>-140</td>
<td>6.6e-6</td>
</tr>
<tr>
<td>Electrochemical Al:ZnO 1 mA/cm$^2$ Pre-Anneal</td>
<td>0.066</td>
<td>0.00015</td>
<td>-42</td>
<td>2.3e-7</td>
</tr>
<tr>
<td>Electrochemical Al:ZnO 1 mA/cm$^2$ Post-Anneal</td>
<td>0.011</td>
<td>0.00075</td>
<td>-88</td>
<td>1.3e-5</td>
</tr>
<tr>
<td>Chemical Codeposition ZnO[153]</td>
<td>35</td>
<td>10</td>
<td>-245</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Chemical Codeposition Zn$<em>{0.97}$Al$</em>{0.03}$O[153]</td>
<td>20</td>
<td>125</td>
<td>-225</td>
<td>0.02</td>
</tr>
<tr>
<td>Ball Sintering ZnO[53]</td>
<td>24</td>
<td>0.4</td>
<td>-300</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Ball Sintering Zn$<em>{0.98}$Al$</em>{0.02}$O[53]</td>
<td>18</td>
<td>2.4</td>
<td>-180</td>
<td>0.018</td>
</tr>
<tr>
<td>RF Plasma + Sintering ZnO[62]</td>
<td>37</td>
<td>10</td>
<td>-350</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>RF Plasma + Sintering Zn$<em>{0.98}$Al$</em>{0.02}$O[62]</td>
<td>27</td>
<td>750</td>
<td>-40</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Microwave-Activated Thermal Decomposition ZnO[32]</td>
<td>7</td>
<td>&lt;10</td>
<td>-490</td>
<td>N/A</td>
</tr>
<tr>
<td>Microwave-Activated Thermal Decomposition Zn$<em>{0.98}$Al$</em>{0.02}$O[32]</td>
<td>2</td>
<td>&lt;20</td>
<td>-280</td>
<td>N/A</td>
</tr>
</tbody>
</table>

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Chapter 5

Conclusions and Future Work

The thermoelectric potential of electrochemically grown, aluminum doped ZnO was studied. The lattice thermal conductivity was modelled using molecular dynamics to determine which nanostructural features would provide reductions in thermal conductivity while minimizing their effects on electrical conductivity. These modelling results combined with classical electrical conductivity estimation indicated that the greatest improvements in thermoelectric performance could be realized with nanovoided and heterostructured ZnO-based materials. Although nanoscale features with the dimensions used in the MD simulations could not be realized experimentally, these structures were still chosen for experimental synthesis as they have been otherwise independently confirmed as effective for improving thermoelectric performance in other material systems.

Growing ZnO and Al:ZnO films with sufficient thickness for direct method characterization required a rigorous examination of established electrochemical growth methods for preparing ZnO thin films, leading to contributions that enabled the development of thicker, higher quality films. These changes included using zinc metal counter electrodes, removing the reference electrode and focusing on galvanostatic deposition, and vertically orienting the substrates a centimetre above the bottom of the beaker during growth. The chemical doping of the films using aluminum was also characterized in detail to produce films with controlled amounts of aluminum integrated throughout the film. Poor aluminum dopant activation and strong evidence for the integration of hydroxide into the films were two new challenges uncovered during the experimental work that seriously impacted the thermoelectric performance of the material.

Tools were developed to assist with the modelling, preparation, and characterization of the films. To help facilitate rapid exploration of the parameter space associated with small nanostructural modifications to a material, LVDOS-EMD was developed, validated with modelled silicon nanostructures, and used to study nanovoided and cored structures for their optimal
structural configurations. ZnO films of varying current densities and dopant concentrations up to 95 µm thick with and without nanoscale features were grown using a custom designed galvanostat. The films showed good purity, strong (002) crystal alignment, and consistent surface morphology. A process of releasing the gold film from a gold/chromium coated glass slide under pH neutral or basic conditions was developed and realized using chromium etching. The etching process was characterized at different temperatures, applied potentials, and anion concentrations for the purpose of generalizing the methodology for MEMS and other microscale device fabrication. Over 100 ZnO films were grown with 20 films etched free from their substrates for thermoelectric characterization.

A reusable, direct measurement apparatus was designed, constructed, calibrated, and used to characterize the thermoelectric performance of the films. The apparatus was designed and constructed specifically to accommodate the measurement of thin films by using a new technique of coating electrodes with very thin layers of highly conductive liquid metal. Thermoelectric measurements revealed that all grown, annealed, films presented extremely low thermal conductivity (<0.1 W m$^{-1}$ K) and reasonable Seebeck coefficients (−50 µV K$^{-1}$ to −300 µV K$^{-1}$). The doped films’ electrical conductivity (~0.7 mS/cm at room temperature) represents the greatest limitation in thermoelectric performance, restricting the $ZT$ of the materials to $1.3 \times 10^{-5}$ at room temperature, significantly below Al:ZnO films produced using other methods.

5.1 Contributions

5.1.1 Modelling

- Developed a method, LVDOS-EMD, for rapidly studying the impact of nanostructural changes on thermal properties of nanoscale materials using molecular dynamics, the velocity autocorrelation function, and a new method for estimating vibrational mean free path using localized vibrational density of states.

- Performed Mueller-Plate and LVDOS-EMD studies on a variety of ZnO structures to determine the potential gain in thermoelectric material performance those structures would provide. Based on these simulations, nanovoided and heterostructured bulk materials are worth greater consideration as thermoelectric materials than straight and hollow nanowires provided that they can be synthesized due to a 3-5×
5.1. Contributions

reduction in relative thermal conductivity when adjusted for effective cross-sectional area.

5.1.2 Experimental Growth and Etching

- Determined that using an inert counter electrode, such as platinum, rather than a Zn-based electrode causes acidification of the ZnO growth solution when using Zn(NO$_3$)$_2$, preventing thick film (>10 µm) deposition of ZnO onto a gold substrate.

- Characterized the effect of using a reference electrode for ZnO thick film electrochemical deposition, determining that using a Ag/AgCl electrode leaks chloride into the growth solution which is absorbed by the growing film, impacting its crystallinity, morphology, opacity, electrical resistance, and surface roughness.

- Successfully grew the thickest known ZnO films (>95 µm) using a nitrate-based, electrochemical method.

- Explored the process of chemical aluminum doping of ZnO films during growth and developed a new experimental method for the regular, controlled introduction of aluminum into the film.

- Developed a new electrochemical etching technique to allow for the freeing of nanoscale gold film from glass slides under pH neutral or basic conditions. Successfully used this method to free ZnO thick films from glass slides to enable thermoelectric characterization.

5.1.3 Thermoelectric Characterization

- Directly compared common thermal/electrical interface materials and concluded that GaInSn or a close analog was suitable for thin film thermoelectric material characterization using a contact-based direct method.

- Designed, constructed, and calibrated a low cost, direct measurement thermoelectric test apparatus for thin thermoelectric films (tested to 79 µm film thickness).

- Thermoelectrically characterized electrochemically grown, nanovoided ZnO and Al:ZnO films, demonstrating their exceptionally low thermal conductivity. A reasonable Seebeck coefficient was also shown. The
5.2 Future Work

The most critical limitation that must be overcome is the poor electrical conductivity of the material. Numerous potential solutions exist for enhancing the electrical conductivity, such as high temperature annealing, testing activation of other dopants such as gallium, and exploring the growth parameter space to improve crystallinity.

A high temperature anneal of films after growth would encourage the aluminum ions in the film to engage in substitution doping and complete the thermal decomposition of any remaining hydroxides in the film, ideally leaving voids that yield the beneficial reduction in thermal conductivity. Creating a viable film through high temperature annealing is a non-trivial task. Al:ZnO must be annealed at 950°C for 2 hours to preserve the stoichiometric ratio of Zn and O while activating the aluminum dopant[32, 62]. Concurrently improving dopant activation and enhancing crystallinity in the electrodeposited films would require exploring annealing between 950°C and 1800°C (the melting temperature of pure ZnO is 1975°C). Annealing at such high temperatures for extended durations is energy intensive, and many of the benefits of electrochemically depositing the Al:ZnO, such as low energy and equipment cost, dopant concentration control, and nanostructuring could be lost if a high temperature anneal is required. An apparatus to prevent warping of the films during the annealing process would need to be constructed using materials that would not engage in chemical exchanges with the film sample.

The parameter space for ZnO and Al:ZnO films should be further explored for different growth conditions in an attempt to improve electrical conductivity without significantly increasing the thermal conductivity of the films. Depositing films at higher current density, as shown with the 3 mA/cm² films, warrants further investigation as these films demonstrate a superior Seebeck coefficient relative to those grown at lower current densities. Small variations in the growth parameters of the films have a large impact on their thermoelectric properties. A study on controlling oxygen doping of the films during growth would also be valuable.

The modelling of synthesizable nanostructures was not exhaustive. Additional nanostructured shapes could be considered using the described mod-
5.2. Future Work

elling methodologies. LVDOS-EMD and NEMD can be used to examine the potential of roughened ZnO nanowires, as well as stacked ZnO platelets and tree formations[40]. These alternative nanostructures may yield interesting improvements in thermoelectric performance. A variety of heterostructures should be considered as well, including other material systems such as aluminum oxide or gallium nitride within the superlattice, as they would provide interesting opportunities for bandstructure engineering. GaN also has lattice parameters that closely match ZnO as well as a tolerance for high temperatures making it an excellent mechanical pairing for the oxide.

The thermoelectric test apparatus demonstrated remarkable utility considering the low cost of components. For longer term, reliable use, several modifications to the design are recommended. The base plate should be replaced by stainless steel or another stiff material that is impervious to gallium. Reducing the flexure of the plate would allow probe support designs that provide better control of the force applied to the DUT. The heater probe could be improved using clean room techniques and higher conductivity materials, with a concept design shown in Appendix B.4. Better mechanical interconnects that place less stress on wires throughout the vacuum region of the apparatus would also improve system longevity. Although the vacuum proved sufficient for preventing convective thermal losses, long periods of operation at high temperature did permit residual oxygen in the air to oxidize some of the materials in the heater probe, such as the nichrome wire. Operating at a higher vacuum would improve the longevity of the system. The test apparatus could also be improved by verifying its performance using other known thermoelectric materials with varying degrees of surface roughness and thermoelectric properties.

Provided that the challenges discussed herein can be overcome with little additional cost, electrochemically grown Al:ZnO has the potential to yield an inexpensive, environmentally friendly, and high $ZT$ material. Modelling indicates that the thermal conductivity of monocrystalline bulk Al:ZnO can be kept low (reduced by over 50× vs. bulk) while maintaining approximately 70% of the electrical conductivity of the material, with experimental results illustrating that significant reductions in thermal conductivity are indeed achievable. The flexibility of electrochemical growth could also enable the fabrication of large thermoelectric modules where the materials are grown directly on the module substrate, and interfaces are electrochemically deposited with the application of some masking between growth stages. The high Seebeck coefficient and temperature performance of oxides gives them the potential to be some of the highest efficiency thermoelectric materials available, and their chemical stability increases their suitability and relia-
5.2. Future Work

bility for future thermoelectric generators. Electrochemically grown, nanos-
structured Al:ZnO remains a promising low-cost thermoelectric material,
but further improvements in film consistency and electronic conductivity are
necessary before achieving commercially viable thermoelectric performance.
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Appendix A

Supplemental Results

A.1 Electronic Quantum Modelling

A consistent modelling method that directly incorporates quantum effects would be ideal for modelling electronic behaviour. Quantum modelling of electronic behaviour in nanostructures generally involves combining an ab initio solver using Hartree Fock (HF) or density functional theory (DFT) with various approximations such as the local-density approximation (LDA) to determine material bandstructure with a transport solver such as non-equilibrium Green’s Function (NEGF) formalism, boundary wave function (WF) formalism, quantum transmission boundary method formalism (QTBM), or the boltzmann transport equation [210, 211]. Solving systems of atoms involving thousands of atoms for all electronic states is extremely computationally intensive, meaning that large nanostructured systems require approximations to simplify the computations. Tools such as Abinit and the Spanish Initiative for Electronic Simulation with Thousands of Atoms (SIESTA) [212] are capable of solving DFT problems using pseudopotentials, which reduce the number of bonding electrons involved in quantum calculations.

Significant exploration with tools such as SIESTA, NEMO5 from Purdue University, BoltzTraP for BTE transport calculations [213], Opium for generating pseudopotentials, and Smeagol did not yield a model suitable for efficiently modelling the electronic quantum behaviour of ZnO nanostructures. ZnO presents a unique challenge when working with pseudopotentials as core electrons in the $3s^2$ and $3p^6$ orbitals still influence the bonding energies between zinc and oxygen atoms within the lattice. Attempts to include these orbitals in the valence shell of the pseudopotentials did not yield models that, once relaxed, produced both lattice spacing and bandstructure consistent with ZnO experimental results. Others have succeeded in generating models involving bulk ZnO but at a much higher computational cost [214, 215]. An alternative solution, LDA+SIC (local-density approximation with self interaction correction) as implemented by Smeagol was able to efficiently produce ZnO models with either correct bandstructure.
or correct lattice constants, but both could not be concurrently produced with the available pseudopotentials\cite{216,217}. Figure A.1 shows the results of ZnO bulk and nanowire bandstructure calculated using Smeagol and its comparison to bulk ZnO simulated by others. Quantum Modelling of ZnO was therefore not further pursued in this work.

A.2 Other ZnO Growth Considerations

In addition to studying the effects of the electrodes used during growth, many other considerations were also examined to improve consistency between samples and overall film quality. The factors considered in this section were examined under a variety of experimental configurations following the equipment and methodology described in Section 3.2.

A.2.1 Solution Stirring During Growth

Stirring involves either agitating the growth solution surrounding the substrate using a magnetic stirrer, or agitating the substrate itself through a mechanical armature. Stirring the solution using a small stir rod and hot-plate magnetic stirring mechanism at 300 RPM increased film growth rate by 1.5× by improving the replenishment rate of nitrate at the substrate surface. The improvement in film growth rate was measured during potentiostatic depositions as a sharp increase in deposition current for a given reference potential. The increase persisted only as long as the solution was agitated. A similar increase in current was also noted when the substrate was rotated 180° back and forth along the length of the substrate using a servo mechanism at a three second period.

To test the impact of agitation on the quality of the film, a stir rod was placed in close proximity to one section of a large growth substrate where 3 cm of substrate was located beneath the surface of the solution. A 2 hour deposition under these conditions yielded a typical ZnO film near the surface of the growth solution and very little film on the substrate near the stir rod. A similar effect was noted when regularly agitating the substrate. Although deposition current does increase, the hydroxide produced by the electrochemical reaction was moved from the surface of the substrate due to the strong fluid currents at the surface, preventing the thermal decomposition of ZnO onto the substrate, as shown by (3.4). As a result of this observation, regular stirring during electrodeposition was not used. A stir rod was used to mix the Zn(NO$_3$)$_2$ solution during solution warm up, but it was then disabled.
A.2. Other ZnO Growth Considerations

Figure A.1: Bandstructures from LDA+SIC simulations of a) bulk ZnO, and b) a hexagonal nanowire composed of ZnO segments of 4 unit cell length. The inset in a) shows bulk ZnO bandstructure calculated using LDA+SIC as a reference [47].
A.2.2 Bubble Formation on Film Integrity

Heating water to 80$^\circ$ C for long durations causes the formation of bubbles within the solution. The bubbles formed on all surfaces during deposition, including the bottom and walls of the beaker and the surface of the substrate. The bubbles on the substrate could also have resulted from the formation of hydrogen gas due to electrolysis near the substrate surface. Once in place, the bubbles prevented the deposition of ZnO by preventing the growth solution from accessing the surface of the substrate. For this reason, bubbles had to be regularly removed from the substrate by either briefly agitating the substrate or by using a syringe to fire a jet of growth solution at the substrate. The latter method proved to more consistently disburse collected bubbles and did not place as much stress on the electrical interconnects leading to the substrate surface. Correspondingly, electrode-positions involved spraying the substrate once every 1-4 hours depending on need. The effect of bubbles left on the surface can be seen in Figure A.2.

![Microscope image showing a chloride-contaminated (for better contrast) ZnO film where bubbles were no longer removed once the deposition reached 50% completion.](image-url)
A.2. Other ZnO Growth Considerations

A.2.3 Substrate Orientation and Location

The effect of substrate orientation was studied as hydrothermal ZnO depositions have indicated the importance of the substrate orientation for high quality films[66]. ZnO growth was attempted with substrates aligned vertically, horizontally facing up, and horizontally facing down. Samples aligned vertically, which is typical, presented minimal bubbles formation and high quality ZnO films. The majority of the samples grown in this work were grown vertically. Measurements indicated that vertically grown films were not deposited evenly along the substrate. The bottom of the substrate invariably produced film thicknesses up to twice that of films grown on the substrate 2 cm higher. The gradient in thickness was much less when the solution was stirred, suggesting that a natural ion gradient forms in the solution, with nitrates and zinc ions presenting at higher concentrations closer to the bottom of the beaker. In support of this hypothesis, films grown at the very bottom of the beaker were much darker in colour and more erratic in shape than films grown even 5 mm above the bottom of the beaker. For this reason, high quality films were all grown at least 5 mm above the bottom of the beaker, demonstrating even colouration and thickness across their entire surface.

Films oriented horizontally facing up were generally low quality. Some precipitation occurs during long depositions, typically in the form of slough from the zinc electrode. When facing up, the substrate can catch particles precipitated from the solution, causing irregularities in the shape and colour of the film. When facing down, very high quality films were produced, particularly when the counter electrode was located above the film allowing the ions to sink and encounter the substrate. In this configuration, bubble formation is a significant challenge. Whereas bubbles will slide off a vertically aligned or top facing substrate, when facing down bubbles would rapidly collect, requiring frequent dislodgement and interfering with the consistent growth of the film. For this reason, horizontal, downward facing growth was not typically used. Vertical alignment of the substrate also allowed for placing the reference electrode very near to the surface of the substrate, providing more accurate reference potential measurements.

A.2.4 ZnO Growth Denouement and Cooling

After the completion of growth, the hotplate was immediately turned off and the beaker containing the sample was removed to cool. Removing the sample immediately after the deposition completed caused cracks to form in the ZnO
A.3. Alternative ZnO Substrate Release Methods

film as the film cooled significantly faster than the underlying substrate. To
minimize damage to the film, the beaker containing the growth solution and
the sample was left until it returned to room temperature before removing
the sample. The sample was then cleaned using a hand-pressurized jet of
distilled water from a squeeze bottle. No ultrasonication or other chemical
cleaning was necessary. The film was either left to air dry or compressed
nitrogen gas was used to expedite drying the film with no apparent effects
on the quality or surface properties of the film.

A.3 Alternative ZnO Substrate Release Methods

In order to form a low impedance electrical and thermal pathway to both
sides of the ZnO film, the growth substrate must either have a high ther-
amal and electrical conductivity or the film must be removable. Mechanical
methods were explored for removing the films from rigid substrates after
growth using tape or shearing action. Graphite as a flexible substrate was
also examined. Chemical and electrochemical methods for releasing the film
were also examined in detail to determine their feasibility and are discussed
in Section 3.5.

A.3.1 Mechanical Removal

Mechanical removal of the film involved separating the film from the growth
substrate through the application of mechanical force. The most direct
method for removing the ZnO involved applying conventional Scotch tape
to the surface of the film and drawing the tape away. This method was very
successful at removing film from the substrates, particularly if the film had
poor adhesion. Films presented lower adhesion when they were removed
immediately after growth as discussed in Section A.2.4 or were grown with
high concentrations of contaminants such as chloride. The bond between
the gold and ZnO could also be weakened at the beginning of deposition
if heightened current densities of 3 mA/cm$^2$ were applied for 10 minutes.
Although removing film using tape was practical for some experimental in-
vestigations, such as ultraviolet spectrography, the strong adhesion and
flexibility of the tape would invariably lead to the destruction of the film,
leaving only powdered remnants.
A.3. Alternative ZnO Substrate Release Methods

A.3.2 Growth on Graphite

An alternative to removing the film from the substrate is selecting a flexible substrate that can be incorporated into the thermoelectric module along with the ZnO film. Graphite thin films have very high thermal and electrical conductivities. The Panasonic PGS series of pyrolytic sheets were also available in 10µm thick varieties at reasonably low cost. The films were flexible and had a slightly rough or thatched surface. Several experiments were conducted growing ZnO on graphite substrates. The graphite was taped to a glass slide to provide a flat surface and the experimental conditions were otherwise similar to those presented in Section 3.2. Some precedents exist in literature for successfully electrodepositing ZnO on graphite[218].

Many films were grown and characterized. XRD results of a ZnO-on-graphite film are shown in Figure A.3. Additional peaks inconsistent with either graphite or ZnO were found in all grown samples. The additional peaks varied between samples and did not correspond to any materials within the available NIST database. When the ZnO film was removed from the graphite substrate after growth and the components were tested separately, unidentified peaks were found in both the graphite and the ZnO, suggesting that the contaminants are formed on or near the graphite surface during deposition. It was also noted that mechanically removing the ZnO from the graphite typically resulted in some carbon remaining adhered to the underside of the ZnO film.

SEM images were also taken of the graphite surface and resulting ZnO as shown in Figure A.4. These images show the roughness of the graphite surface and the corresponding sloped hills and valleys on the surface of the ZnO film. Due to the rough nature of the surface and impurities during growth, the ZnO crystals did not properly align leading to anomalous structures throughout the ZnO lattice, an example of which is shown in Figure A.4c. The films also had poor adhesion to the substrate and would readily break free, indicating low electrical and thermal contact. Despite varying experimental parameters such as growth temperature and substrate pretreatment, high quality ZnO films with good substrate adhesion and negligible contamination were not successfully produced.
A.4 Experimental Synthesis of Additional ZnO Structures

In addition to nanovoided bulk structures, attempts were made to grow other structures that demonstrated good theoretical performance as thermoelectric candidates.

A.4.1 Template Assisted Growth

Although ZnO nanowires can be synthesized in a wet environment either through hydrothermal or electrochemical deposition, their aspect ratios and lengths are very limited and typically yield 10µm long, 700nm thick nanowires\cite{40, 46, 66, 75, 218-220}. Templated assisted growth involves growing ZnO through the pores of a stiffer template material such as polycarbonate or alumina\cite{86, 221}. The former are fabricated from 5 to 15µm polycarbonate films that are bombarded by radiation of a known velocity and energy that tunnels holes through the polycarbonate with a consistent diameter and known density. These holey polycarbonate membranes are often used as filters in biological applications. To use them for electrochemical growth, a thin layer of gold is deposited on one side of the template, which then serves as the cathode in an electrochemical deposition. ZnO is

Figure A.3: XRD measurements of a ZnO-on-graphite film along with gold and ZnO reference patterns are shown.
A.4. Experimental Synthesis of Additional ZnO Structures

Figure A.4: SEM measurements of a) the graphite surface, b) ZnO grown on graphite, and c) anomalous structures embedded into the film.
formed in the cavities in the template, forming nanowires bounded by the dimensions of the holes. Once the holes have been filled with electrochemically deposited ZnO, a separate deposition procedure can be used to deposit the top electrode on the structure, securing the nanowires at both ends. The template can then be dissolved, leaving a forest of vertically aligned nanowires interconnected at both ends.

Figure A.5 shows the result of copper-coated ZnO nanowires extending from the top of a 100 nm hole diameter polycarbonate template. One side of the template was sputter coated with 50 nm of gold with the templates at an angle to prevent filling the holes with gold. Potentiostatic deposition at $-1.0 \text{ V}$ was then performed in a standard 80°C solution of 0.1 M Zn(NO$_3$)$_2$ for 6 hours. The substrate was then immersed in a copper sulphate solution with copper electrode for an additional hour of electrodeposition in an attempt to form a continuous, interconnected film on the surface of the template. The copper did not fully interconnect the nanowires, indicating that a different deposition method would be necessary. The polycarbonate film was etched in a 1 M NaOH solution after the SEM images were taken, but rather than entirely dissolve the template, the polycarbonate formed a gel that warped and destroyed the nanowires.

Thicker substrates on either ends of the nanowires would be necessary to achieve the mechanical strength necessary to remove the template without damaging the nanowires. Smaller diameter nanowires with larger aspect ratios would also be required to achieve a significant reduction in thermal conductivity, further increasing the risk and reducing the yield of thermoelectric material fabrication. Due to the slow growth rate, low nanowire density, clean room fabrication steps, and mechanically fragile growth product, this methodology was not further pursued.

### A.4.2 Heterostructural Growth

Growing heterostructure films involves depositing ultra thin layers of two or more materials in sequence. Superlattice nanowire heterostructures have been theoretically and experimentally demonstrated using Si/Ge[21][22][25], Si/SiGe[222], Kr/Ar[223], AlN/GaN[224], BiTe/BiSbTe[113], and others. Forming a heterostructure using the electrochemical process has been successfully demonstrated by varying the applied deposition potential to preferentially select the elements for deposition[113]. With the Al:ZnO material system, possible candidates include heterostructures of ZnO/AlO and ZnO/Zn. As discussed in Section 3.4.2.2, aluminum preferentially deposits to zinc where $V_{ref}$ is between $-0.4 \text{ V}$ and $-1.0 \text{ V}$ vs. Ag/AgCl. Due to this
Figure A.5: SEM images taken at 20 kV showing ZnO nanowires potentiostatically grown at $V_{\text{ref}} = -1.0$ V emerging from the top of a polycarbonate template. The nanowires were then electrochemically coated with copper in a Cu(SO$_4$) solution in an attempt to develop a film.

selectivity, and provided that a consistent level of a aluminum dopant can be maintained within the solution, the potential-driven selection between ZnO/AlO is plausible by varying the applied potential between $-0.5$ V for AlO deposition and $-1.0$ V for doped Zn deposition. AlO is a strong insulator with a large bandgap, meaning that either very thin layers or high dopant concentrations would be necessary to maintain the desired electrical conductivity of the material. Due to this constraint, AlO was not selected as the preferred heterostructure for investigation.

The ZnO/Zn heterostructure can also be selected by varying the applied
A.4. Experimental Synthesis of Additional ZnO Structures

potential during electrodeposition. Applying a high potential ($V_{ref} > 1.0 \text{ V}$) begins to deposit zinc metal directly onto the cathode as the thermal decomposition step in the formation of ZnO is rate limiting. Figure A.6 compares XRD measurements of a conventionally grown ZnO film with a heterostructure grown galvanostatically by swapping applied current density between 1 mA/cm$^2$ and 10 mA/cm$^2$ every 10 C of charge transferred. The XRD data shows that the highly directional growth of the ZnO crystal is disrupted with growth occurring along many more crystal axes. Zinc metal is also visible within the XRD data, confirming that some pure Zn metal was deposited in the process.

![XRD plot comparing conventionally electrochemically grown ZnO with a ZnO heterostructure grown by swapping applied current density from 1 mA/cm$^2$ to 10 mA/cm$^2$ every 10 C of charge transferred.](image)

Figure A.6: XRD plot comparing conventionally electrochemically grown ZnO with a ZnO heterostructure grown by swapping applied current density from 1 mA/cm$^2$ to 10 mA/cm$^2$ every 10 C of charge transferred.

Visually, the ZnO/Zn heterostructured film was translucent and very inconsistent. Rather than laying down contiguous sheets of Zn and ZnO, high current Zn deposition favoured growing outwards from several points on the ZnO film, creating large, plated structures of Zn that were subsequently covered by ZnO and additional layers of Zn. These structures were
A.4. Experimental Synthesis of Additional ZnO Structures

not continuous across the surface of the film, resulting in a very poor superlattice structure. The SEM images are shown in Figure A.7. In the figure, segments of ZnO can be seen capped with zinc metal, creating either mushroom (Figure A.7a) or pine cone (Figure A.7b) like structures. Although these examples do illustrate the intention behind a heterostructure, the poor uniformity across the entire surface of the substrate reduces the practical utility of the methodology for thermoelectric applications. Forming and using ZnO/Zn superlattice nanowires may be more functional as uniformity over a large surface area is not as critical.

Figure A.7: SEM images taken at 15 kV showing the cross-section of a heterostructured ZnO/Zn film. The object seen in the figure is a protrusion from the film and is representative of many other protrusions along the surface.
Appendix B

Thermoelectric Tester Design

B.1 Front Panel
Figure B.1: Labview Front Panel of Thermoelectric Tester Application.
B.2. Labview Programming

B.2 Labview Programming
B.3 Plate Design
Figure B.2: Drawing of Thermoelectric Test Apparatus enclosure base plate. 1/4" aluminum was used.
B.4. Microheater Design

B.4 Microheater Design

Although this design was considered for microfabrication, it was never implemented. It is included here as a reference should others wish to replicate the work with a higher quality, better performing heater element.
Figure B.3: Concept mock-up of a thin film heating element based on a microfabricated silicon wafer. A thermocouple is inserted into the back groove of the substrate.
KOH etch depth of 0.25 mm (for 500 μm wafer) or 0.7 mm (for 1 mm wafer) at deepest point:
- Given 30% solution of KOH at 80 degrees C
- Etch rate of ~80 μm/hour

The mask should be tolerant to within +/- 1 mm.
KOH etch depth of 0.25 mm at deepest point:
- Given 30% solution of KOH at 80 degrees C
- Etching requires 3 hours (etch rate of ~80 um/hour)

The mask should be tolerant to within +/-1 mm. Alignment with the top should be tolerant within +/-2 mm.
SiO2 deposition or growth of 100 - 300 nm of SiO2 over total area. The area for SiO2 deposition must be at least the dimension of the box indicated.

Figure 2: SiO2 Growth
Evaporation or sputtering of chromium onto the substrate

- Target thickness of chromium layer is 100 +/- 20 nm
- Mask tolerance of 10 um in all directions permitted

100 um wide strips of chromium should be deposited between two larger chromium plates, all on SiO2.
Gold should be applied until between 300 - 500 nm thick using evaporation or sputtering. Mask tolerance of +/- 1 mm is acceptable.

Figure 4: Gold Deposition
PECVD deposition of 200 - 400 nm of SiO2 over unmasked area. +/-2 mm mask tolerance is acceptable for SiO2 deposition.
The area not cut out may be discarded. It is better if excess material is included (cut is larger than indicated) than cutting into the device.
Appendix C

Thermoelectric Tester Source

C.1 Firmware

A standard Netburner MOD5282 development kit was used to form a bridge between Ethernet and SPI/I2C temperature sensors. The following code was developed using the NBEclipse IDE and SDK.

```c
#include "predef.h"
#include <stdio.h>
#include <string.h>
#include <ctype.h>
#include <startnet.h>
#include <serial.h>
#include <iosys.h>
#include <utils.h>
#include <ip.h>
#include <tcp.h>
#include <autoupdate.h>
#include <command.h>
#include <taskmon.h>
#include <stdlib.h>
#include <i2cmaster.h>
#include <networkdebug.h>
#include <pins.h>
#include <qspi.h>

#define SERIALPORT_TO_USE (0) //0 for the main port, 1 for the 10pin aux serial port
#define BAUDRATE_TO_USE (115200)
#define STOP_BITS (1)
#define DATA_BITS (8)
#define TCP_PORT_TO_USE (23) //The Telnet port
```
C.1. Firmware

```c
float sensorData[16];
int dataread[4];

extern "C"
{
    void UserMain( void *pd );
}

/* The User Authentication Callback */
int ProcessAuth( const char *name, const char *pass )
{
    return CMD_OK;
}

void ProcessPrompt( FILE *fp, void *pData )
{
    /* For fun give each session its number in the prompt */
    fprintf( fp, "Channel #1: %.4f (%04x)\n", sensorData[0], dataread[0] );
    fprintf( fp, "Channel #2: %.4f (%04x)\n", sensorData[1], dataread[1] );
    fprintf( fp, "Channel #3: %.4f (%04x)\n", sensorData[2], dataread[2] );
    fprintf( fp, "Channel #4: %.4f (%04x)\n", sensorData[3], dataread[3] );
}

/* The command processing Callback */
int ProcessCommand( const char *command, FILE *fp, void *pData )
{
    if ( command[0] )
    {
        fprintf( fp, "#\%s Sent Cmd[\%s]", pData, command );
    }
```
C.1. Firmware

/* Close the connection if we receive Logout */
if ( stricmp( command, "logout" ) == 0 )
{
    return CMD_CLOSE;
}
return CMD_OK;

void * ProcessConnect( FILE *fp )
{
    const char *prompt;
    fprintf( fp, "Connected: TE Tester Rev3\n" );
    if ( ( int ) ( fp->_file ) == ( SERIAL_SOCKET_OFFSET ) )
    {
        prompt = "Serial0";
    }
    else if ( ( int ) ( fp->_file ) == ( SERIAL_SOCKET_OFFSET + 1 ) )
    {
        prompt = "Serial1";
    }
    else
    {
        prompt = "Telnet";
    }
    /* To test arbitray data tracking return the session number */
    return ( void * ) prompt;
}

void ProcessDisconnect( FILE *fp, int cause, void * pData )
{
    switch ( cause )
C.1. Firmware

{ 
    case CMD_DIS_CAUSE_TIMEOUT:
        fputs("\nTimed out\n", fp);
        break;
    case CMD_DIS_CAUSE_CLOSED:
        fputs("\nGoodBye\n", fp);
        break;
    case CMD_DIS_SOCKET_CLOSED:
        fputs("Socket closed\n", fp);
        break;
    case CMD_DIS_AUTH_FAILED:
        fputs("Authentication failed\n", fp);
        break;
}
}

const char *AppName = "TETester";

const char sensAddr[4] = {0x48, 0x49, 0x4a, 0x4b};

float getSensor( int i )
{
    BYTE ret[2];
    signed short int data;

    ret[0] = 0x00;
    ret[1] = 0x00;
    I2CSendBuf( sensAddr[i], ret, 1, 0);
    I2CRestart( sensAddr[i], I2C_START_READ );
    I2CReadBuf( sensAddr[i], ret, 2, 1);

    dataread[i] = (int)(ret[0]) * 256 + (int)(ret[1]);
    data = (signed short int)(ret[0]) * 256 + (int)(ret[1]);
    return (float)(data) / 128.0; //Returns in degC
}

float getSensorSPI( int i )
{
C.1. Firmware

```c
{    
    signed long int ret;
    float Text, Tint;

    // Acquire data
    if( i < 2 )
        J2[40] = 0;
    else
        J2[30] = 0;

    QSPIStart( NULL, (BYTE*)(&ret), 4, NULL);

    // Wait until complete
    while(!QSPIdone());

    J2[30] = 1;
    J2[40] = 1;

    // Calculation
    Text = (float)(ret >> 18) / 4;
    Tint = (float)((ret & 0x0000ffff) >> 4) / 16;
    if( !(i & 0x1) )
        // External temperature channel
        return Text;
    else
        return Tint;
}

void initSPI()
{
    J2[25].function(PINJ2_25_SPI_CLK);
    J2[27].function(PINJ2_27_SPI_DIN);
    J2[28].function(PINJ2_28_SPI_DOUT);
    J2[30].function(PINJ2_35_GPIO);
    J2[40].function(PINJ2_40_GPIO);
    J2[30] = 1;
    J2[40] = 1;

    QSPIInit(2000000, 32, 0, 1, 1, 1, TRUE, 5, 5);
}
```
void initI2C()
{
    I2CInit( 0x15 ); //Should be 100 kHz
    OSTimeDly( 10 );

    //Initialize each of the temperature devices
    //Config reg (addr 0x3) = 0x80
    for( int i = 0; i < 4; i++ )
    {
        //Reset the part
        I2CStart( sensAddr[i],
            I2C_START_WRITE );
        I2CSend( 0x2f ); // Address
        I2CStop();
        OSTimeDly( 10 );

        //Setup config
        I2CStart( sensAddr[i],
            I2C_START_WRITE );
        I2CSend( 0x03 ); // Address
        I2CSend( 0x80 ); // Control register value
        I2CStop();
    }
}

void UserMain( void *pd )
{
    InitializeStack();
    OSChangePrio( MAIN_PRIO + 1 );
    EnableAutoUpdate();
    EnableTaskMonitor();
    OSTimeDly( 10 );

    #ifdef _DEBUG
C.1. Firmware

```
InitializeNetworkGDB();
//InitializeNetworkGDB_and_Wait();
#endif

//Close the serial port incase it is already open.
SerialClose( SERIALPORT_TO_USE );

//--Open the serial port
int fdserial = OpenSerial( SERIALPORT_TO_USE,
    BAUDRATE_TO_USE,
    STOP_BITS,
    DATA_BITS,
    eParityNone );

ReplaceStdio( 0, fdserial );
ReplaceStdio( 1, fdserial );
ReplaceStdio( 2, fdserial );

writestring( fdserial, "Starting\n" );

CmdAuthenticateFunc = ProcessAuth; /* No authentication to start */
CmdCmd_func = ProcessCommand;
CmdConnect_func = ProcessConnect;
CmdPrompt_func = ProcessPrompt;
CmdDisConnect_func = ProcessDisconnect;

CmdIdleTimeout = TICKS_PER_SECOND * 3600;
Cmdlogin_prompt = "Logged_in. Rev_0.\n";

CmdStartCommandProcessor( MAIN_PRIO );
CmdAddCommandFd( fdserial, TRUE, TRUE );
CmdListenQuietOnTcpPort( 23, 1, 5 );

// initI2C();
initSPI();

while ( 1 )
{
}
```
C.1. Firmware

    int i;
    for( i = 0; i < 4; i++ )
    {
        OSTimeDly( 2 );
        //
        sensorData[i] = getSensor(i);
        sensorData[i] = getSensorSPI(i);
    }

} //UserMain
C.2 Front Panel

Figure C.1: Labview Front Panel of Thermoelectric Tester Application.
C.3 Labview Programming
<table>
<thead>
<tr>
<th>Probe Temp (C)</th>
<th>Temp 3</th>
<th>Plate Temp (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>12</td>
<td>11.1111</td>
</tr>
<tr>
<td>11.1111</td>
<td></td>
<td>11.1111</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temp 1</th>
<th>12</th>
<th>11.1111</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

-0.001
0.01
-0.01
1500
False
"Power"
KeithPower
KeithPower
Power
True
False
1
False
Appendix D

Matlab Source Files

D.1 Nanowire Area Calculation

```matlab
%area.m - Approximates the cross-sectional area of an arbitrary structure

clear all;
close all;

%Load data
fname = '/data/phonon/ZnOvoidR3V50D17rng1-5x5x200/dumpforce40pre.ZnO';
extractFrame;

index = 1;
levels = 40;  %Granularity of squares
numDots = 20;  %Number of interconnecting dots between nearest neighbours
numAtoms = 10;  %Draw dots between this many neighbours
maxLength = 4;  %Maximum distance (in Å) between nearest neighbours
sliceThickness = 4;  %In Angstroms
sliceIncrement = 1;  %In Angstroms

%Clear existing video files
system('rm video/*.png');

%Generate slice regions
dx = full(squeeze(datax(:,index)));
dy = full(squeeze(datay(:,index)));
dz = full(squeeze(dataz(:,index)));
```
D.1. Nanowire Area Calculation

```matlab
% Nanowire Area Calculation

% More setup
figure('Color', [1 1 1]);
set(gca, 'fontSize', 15);
xlabel('x-axis position (A)');
ylabel('y-axis position (A)');
hold on;

if matlabpool('size') == 0
    matlabpool
end

% Iterate through regions
zIndex = bottom;
k = 1;
while zIndex < top - sliceThickness
    % Prepare/Flatten data
    dx = full(squeeze(datax(:,k)));
dy = full(squeeze(datay(:,k)));
dz = full(squeeze(dataz(:,k)));

    zMin = zIndex;
    zMax = zIndex + sliceThickness;
    disp(sprintf('Doing %.2f to %.2f...', zMin, zMax));
    zIndex = zIndex + sliceIncrement;
    dx((dz<zMin)|(dz>zMax)) = [];
    dy((dz<zMin)|(dz>zMax)) = [];
    dz((dz<zMin)|(dz>zMax)) = [];

    % Delete bad points
    li = find(dx>100|dx<-100|dy>100|dy<-100);
dx(li) = [];
dy(li) = [];
dz(li) = [];

    % Start by finding extreme edges of data
topleft = [min(dx) max(dy)];
```
D.1. Nanowire Area Calculation

botright = [max(dx) min(dy)];
axis([topleft(1) botright(1) botright(2) topleft (2)]);

%Add points between nearest neighbours to help fill in the gaps
dotsx = [];
dotsy = [];
parfor i = 1:length(dx)
    [dist,tmp] = sort(sqrt((dx(i) - dx).^2 + (dy(i) - dy).^2 + (dz(i) - dz).^4));
    for j = 1:numAtoms %Nearest 10 atoms
        if dist(j+1) < maxLength
            %Generate new dots
            dotsx = [dotsx;linspace(dx(i), dx(tmp(j+1)), numDots)'];
            dotsy = [dotsy;linspace(dy(i), dy(tmp(j+1)), numDots)'];
        end
    end
end
dx = [dx;dotsx];
dy = [dy;dotsy];

%Start digging in to determine area
xblocks = 1:(levels);
yblocks = 1:(levels);
xsizes = (botright(1) - topleft(1)) / (levels);
ysizes = -(botright(2) - topleft(2)) / (levels);
tot = 0;
clf;
for x = xblocks
    for y = yblocks
        itopleft = [(x-1)*xsizes -(y-1)*ysizes] + topleft;
        ibotright = [x*xsizes -y*ysizes] + topleft;
        if(find(dx>itopleft(1)&dx<ibotright(1)&
            dy<itopleft(2)&dy>ibotright(2)) )
        end
    end
end

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D.1. Nanowire Area Calculation

```
96       tot = tot + 1;
97       hold on;
98       r = rectangle('FaceColor',[1 0.8
99                   0.8], 'Position',[itopleft(1)
100                  ibotright(2) xsize ysize]);
101       end
102       end
103       totarea(k) = tot * xsize * ysize;
104       areaMsg = sprintf('Area of \%d atom slice is \%.2f
105                     ', length(dx) - length(dotsx), totarea(k));
106       disp(areaMsg);
107       
108       %%{
109           %Plot all atoms
110       hold on;
111       plot(dx, dy, '.');
112       title(areaMsg);
113       set(gcf, 'PaperUnits', 'inches', 'PaperPosition', [0
114                     0 5 5])
115       drawnow;
116       }
117       
118       %Save frame to array
119       print(sprintf('video/area%04d.png', k), '-dpng',
120                     '-r100');
121       k = k + 1;
122       end
123       
124       %Calculate series area adjustment (1/A1 + 1/A2 +
125       ...)^(-1)
126       areaAdj = 0;
127       for i = 1:length(totarea)
128           areaAdj = areaAdj + 1 / totarea(i);
129       end
130       areaAdj = 1 / areaAdj * length(totarea);
```

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D.2 Extract Single Time Frame from LAMMPS Data

%fname must be predefined

timeperstep = 40e-15; % in seconds

% Extra data from file
fp = fopen(fname, 'r');

basetimestep = 0;
umatoms = 0;
bounds = [];
datay = sparse([]);
datay = sparse([]);
dataz = sparse([]);
datamass = sparse([]);
datatype = sparse([]);
datavx = sparse([]);
datavz = sparse([]);
datafy = sparse([]);
datafz = sparse([]);
dataactive = false;

while (~feof(fp))
    s = fgetl(fp);
    if strcmp(s, 'ITEM: TIMESTEP')
        if dataactive == true
            % Write intermediate values to matrices
            tstep = timestep - basetimestep + 1;
            datatype(:,tstep) = inttype;
            datamass(:,tstep) = intmass;
        end
    end
end
D.2. Extract Single Time Frame from LAMMPS Data

```matlab
datax(:,tstep) = intx;  %x
datay(:,tstep) = inty;  %y
dataz(:,tstep) = intz;  %z
datavx(:,tstep) = intvx;
datavy(:,tstep) = intvy;
datavz(:,tstep) = intvz;
%  datafx(:,tstep) = intfx;
%  datafy(:,tstep) = intfy;
%  datafz(:,tstep) = intfz;
break;
end

dataactive = false;
s = fgetl(fp);
if basetimestep == 0
    basetimestep = str2double(s);
end
timestep = str2double(s);
disp(sprintf('Loading timestep: %d', timestep));
continue;
end
if strcmp(s, 'ITEM: NUMBER OF ATOMS')
dataactive = false;
s = fgetl(fp);
umatoms = str2double(s);
continue;
end
if strcmp(s, 'ITEM: BOX BOUNDS xy xz yz pp pp pp ')
dataactive = false;
s = fgetl(fp);
s = regexp(s, ' ', 'split');
bounds(1) = str2double(s(2));
s = fgetl(fp);
s = regexp(s, ' ', 'split');
bounds(2) = str2double(s(2));
s = fgetl(fp);
s = regexp(s, ' ', 'split');
bounds(3) = str2double(s(2));
end
```
D.3. Thermal Conductivity Using Muller-Plathe

```matlab
if findstr(s, 'ITEM: ATOMS')
dataactive = true;
continue;
end

if dataactive
    s = regexp(s, ',', 'split');
    atom = str2double(s(1));
    inttype(atom) = str2double(s(2));
    intmass(atom) = str2double(s(3));
    intx(atom) = str2double(s(4));
    inty(atom) = str2double(s(5));
    intz(atom) = str2double(s(6));
    intvx(atom) = str2double(s(7));
    intvy(atom) = str2double(s(8));
    intvz(atom) = str2double(s(9));
    intfx(atom) = str2double(s(9));
    intfy(atom) = str2double(s(10));
    intfz(atom) = str2double(s(11));
end

fclose(fp);
```

D.3 Thermal Conductivity Using Muller-Plathe

```matlab
% Determine thermal conductivity from stored LAMMPS data
clear all;
close all;

type = 'Zn';
dir = 'Zn05x5x200ts050thermo500';
```

```matlab
cd '/data/phonon';
```
D.3. Thermal Conductivity Using Muller-Plathe

```matlab
fnameProfile = [dir '/tmp.profile'];
fnameLog = [dir '/log.si_flux'];
%fnameProfile = [dir '/tmp.initprofile'];
%fnameLog = [dir '/log.warm_up'];

if type == 'Si'
    timeperstep = 1e-15;  %Time per step in seconds
    len = 400 * 5.43e-10;  %Length in metres
    area = (5 * 5.43e-10) ^ 2;  %Cross-sectional area in m^2
    q = 1.60217646e-19;
else
    a = 3.219e-10;
    c = 5.366e-10;
    timeperstep = 0.5e-15;
    len = 200 * c;
    uc = 5; area = sqrt(3) * (a * uc / 2) ^ 2 * 6;  %Hex nanowire
    q = 1.60217646e-19 * 0.04336;
    % q = 1.60217646e-19;
end

%Load data from file
disp('Loading data from file...');

fp = fopen(fnameProfile, 'r');
step = [];
stepnum = 0;
data = [];
datanum = 1;
while (~feof(fp))
    s = fgetl(fp);
    if s(1) == '#'
        continue;
    ```
D.3. Thermal Conductivity Using Muller-Plathe

```matlab
end

r = regexp(s, ',' ,'split');
if length(r) == 2
    stepnum = stepnum + 1;
    % if(stepnum == 4001 )
    % break;
    % end
    step(stepnum) = str2double(r(1));
    datanum = 1;
end
if length(r) == 6
    data(1,datanum,stepnum) = str2double(r(4));
    data(2,datanum,stepnum) = str2double(r(5));
    data(3,datanum,stepnum) = str2double(r(6));
    datanum = datanum + 1;
end
s = size(data);
datanum = s(2);
stepnum = s(3);
step = step - step(1) + (step(2) - step(1));  % Removing starting offset
fclose(fp);

% Now to the flux file to acquire kinetic energy transfer
fp = fopen(fnameLog, 'r');
logdata = [];
logdatanum = 1;
while(~feof(fp))
    s = fgetl(fp);
    r = regexp(s, ',' ,'split');
    if (length(r) > 5) && strcmp(r{1}, '')
        % Strip whitespace
        r(find(strcmp(r, ''))) = [];
        logdata(1,logdatanum) = str2double(r(2));
        logdata(2,logdatanum) = str2double(r(3));
```
D.3. Thermal Conductivity Using Muller-Plathe

logdata(3,logdatanum) = str2double(r(4));
logdata(4,logdatanum) = str2double(r(5));
logdata(5,logdatanum) = str2double(r(6));
logdatanum = logdatanum + 1;
end
end
logdatanum = logdatanum - 1;
close(fp);

% Restructure data (ugly!)
disp('Preparing data...');
for i = 1:stepnum
    for j = 1:datanum
        Ncount(i,j) = data(2,j,i);
        temp(i,j) = data(3,j,i);
    end
end

% Plotting results
disp('Plotting results...');
x = linspace(0, len, datanum) * 1e9;
y = step * timeperstep * 1e12;
figure('Color', [1 1 1]);
set(gca, 'fontsize', 15);
contourf(x, y, temp, 50, 'edgecolor', 'none');
xlabel('Position [nm]');
ylabel('Timestep [ps]');
colorbar;

figure('Color', [1 1 1])
contourf(x, y, Ncount, 50, 'edgecolor', 'none');
set(gca, 'fontsize', 15);
xlabel('Position [nm]');
ylabel('Timestep [ps]');
colorbar;

Temp
figure
D.3. Thermal Conductivity Using Muller-Plathe

```matlab
%for i = 2:length(y)
  plot(x,temp(i-1,:), 'b','linewidth',2);
  hold on
  plot(x,temp(i,:), 'b--');
  axis([0 400 240 360]);
  hold off
  i
  pause(1);
end

%Computations
disp('Performing computations...');

%Average over time to get temperature gradient plot
  ttemp = sum(temp) / size(temp, 1);
  figure('Color', [1 1 1]);
  set(gca, 'fontsize', 15);
  plot(x, ttemp, 'linewidth', [2.0]);
  xlabel('Position [nm]');
  ylabel('Average Temperature (K)');

%start = floor(0/8 * datanum + 1);
%stop = floor(4/8 * datanum + 1);

%Method 1
  coeffs = polyfit(x(start:stop) * 1e-9, ttemp(start: stop), 1);
  ctemp = polyval(coeffs, x * 1e-9);
  hold on;
  plot(x, ctemp, 'r--', 'linewidth', [2.0]);
  thermgrad = coeffs(1);

%Now the calculation of thermal conductivity
  ketotal = (logdata(5,logdatanum) - logdata(5,1)) * q
  ;
  timetotal = max(logdata(4,:)) * timeperstep;
  heatflow = ketotal / timetotal; %Factor of 2 for periodicity
  kappa = heatflow / 2 / area / thermgrad; %in W/m/K
```

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D.4. Si Nanowire/Bulk Creation

avgtemp = mean(ttemp);

% Second slope
start = floor(4/8 * datanum + 1);
stop = floor(8/8 * datanum);
coeffs = polyfit(x(start:stop) * 1e-9, ttemp(start:stop), 1);
ctemp = polyval(coeffs, x * 1e-9);
thermgrad = -coeffs(1);

% ketotal = (logdata(5,logdatanum) - logdata(5,1)) * q;
% timetotal = max(logdata(4,:)) * timeperstep;
heatflow = ketotal / timetotal; % Factor of 2 for periodicity
kappa2 = heatflow / 2 / area / thermgrad;

disp(sprintf('Thermal gradient: %.2e K/m', thermgrad));
disp(sprintf('Heat flow: %.2e W', heatflow));
disp(sprintf('Area: %.2e m^2', area));
disp(sprintf('Total duration: %.2e s', step(stepnum) * timeperstep));
disp(sprintf('Thermal conductivity 1: %.2f W/K/m', kappa));
disp(sprintf('Thermal conductivity 2: %.2f W/K/m', kappa2));
disp(sprintf('Average temperature: %.2f K', avgtemp));

D.4 Si Nanowire/Bulk Creation

% Generate Si crystal lattice
clear all
close all

% Parameters
a = 5.43; % Lattice spacing in A
numx = 3; % Number of unit cells along x axis
D.4. Si Nanowire/Bulk Creation

numy = 3;  % Number of unit cells along y axis
numz = 20;  % Number of unit cells along z axis
roughen = false;
roughperiod = 10*a;  % Period of breaks in A
roughdepth = 1*a;  %
roughwidth = 1*a;
roughspecial = 0;
ucellx = 5.43;  % Unit cell along x in A
ucelly = 5.43;  % Unit cell along y in A
ucellz = 5.43;  % Unit cell along z in A
celltype = 'FCC';
passivate = false;  % Add hydrogen to passivate generated structure
passlength = 1.46;  % Passivation length (A)
outp = 'out.xyz';  % Output file name
elem = 'Si';
lattice = [0.0 0.0 0.0;0.0 0.5 0.5;0.5 0.0 0.5;0.5 0.5 0.0
0.5 0.0; .25 .25 .25; .25 .75 .75; .75 .25 .75; .75 .75 .25];

% Generate
unitcell = (lattice * a)';

% Build supercell structure, defining where unit cells will go
supercell = [];
m = 1;
for i = 1:numx
    for j = 1:numy
        for k = 1:numz
            x = (i - 1) * ucellx;
            y = (j - 1) * ucelly;
            z = (k - 1) * ucellz;
            supercell(:,m) = [x y z];
            m = m + 1;
        end
    end
end
%Special conditions
if roughspecial == 1 %Add one additional ledge
    for k = 1:(numz * a / roughperiod + 1)
        for i = 1:(numx + 2)
            x = (i - 2) * ucellx;
            y = numy * ucelly;
            z = (k - 1) * roughperiod + roughwidth;
            supercell(:,m) = [x y z];
            m = m + 1;
            y = -1 * ucelly;
            supercell(:,m) = [x y z];
            m = m + 1;
        end
        for i = 1:numy
            y = (i - 1) * ucelly;
            z = (k - 1) * roughperiod + roughwidth;
            x = numx * ucellx;
            supercell(:,m) = [x y z];
            m = m + 1;
            x = -1 * ucellx;
            supercell(:,m) = [x y z];
            m = m + 1;
        end
    end
end

%Assemble list of atoms
atoms = [];
n = 1;
for i = 1:(m - 1)
    for j = 1:length(unitcell)
        x = supercell(1,i) + unitcell(1,j);
        y = supercell(2,i) + unitcell(2,j);
        z = supercell(3,i) + unitcell(3,j);
        atoms(:,n) = [x y z];
        n = n + 1;
    end
end
D.4. Si Nanowire/Bulk Creation

\begin{verbatim}
82  n = n - 1;
83
84  \%Roughen if required
85  if roughen == true
86     rx = 0;
87     ry = 0;
88     rz = -roughperiod;
89     while rz < a * numz
90       rz = rz + roughperiod;
91       x1 = roughdepth;  \%Less than
92       x2 = a * numx - roughdepth;  \%Greater than
93       y1 = roughdepth;
94       y2 = a * numy - roughdepth;
95       atoms(:,(atoms(3,:)>=rz)&(atoms(3,:)<(rz+
96          roughwidth))&((atoms(1,:)<x1|atoms(1,:)>
97          x2)|((atoms(2,:)<y1|atoms(2,:)>
98          y2))) = [];
99     end
100  end
101
102  \%Passivate if required
103  bondlist = sparse([]);
104  hydlist = [];
105  others = [];
106  o = 1;
107  if passivate == true
108     \%Test all atoms for number of close atoms/bonds
109     bondedlength = a / 2;
110     for i = 1:n
111        x = atoms(1,i);
112        y = atoms(2,i);
113        z = atoms(3,i);
114        tmparray = [(x-atoms(1,:)).^2+(y-atoms(2,:))
115                        .^2+(z-atoms(3,:)).^2] <
116                        bondedlength ^ 2;
117        bondlist(:,i) = sparse(tmparray <
118                                bondedlength ^ 2);
119     end
120  end
121
122  \%Fix up bondlist
123  for i = 1:length(bondlist)
124
125\end{verbatim}
D.4. Si Nanowire/Bulk Creation

bondlist(i,i) = 0;
end

%Add hydrogens based on number of bonds
for i = 1:n
    bonds = sum(bondlist(:,i));
    others = full([bondlist(:,i).*atoms(1,:)' bondlist(:,i).*atoms(2,:)' bondlist(:,i).*atoms(3,:)'])';
    others(all(others==0,2),:) = [];
    others = others';
    if(bonds == 3)
        %Add one hydrogen
        vect1 = atoms(:,i) - others(:,1);
        vect2 = atoms(:,i) - others(:,2);
        vect3 = atoms(:,i) - others(:,3);
        newvect = vect1 + vect2 + vect3;
        newvect = newvect * passlength / sqrt((newvect(1,1)^2) + (newvect(2,1)^2) + (newvect(3,1)^2));
        hydlist(:,o) = newvect + atoms(:,i);
        o = o + 1;
    end
    if(bonds == 2)
        %Add one hydrogen
        vect1 = atoms(:,i) - others(:,1);
        vect2 = atoms(:,i) - others(:,2);
        vect1 = vect1 * passlength / sqrt((vect1(1,1)^2) + (vect1(2,1)^2) + (vect1(3,1)^2));
        vect2 = vect2 * passlength / sqrt((vect2(1,1)^2) + (vect2(2,1)^2) + (vect2(3,1)^2));
        hydlist(:,o) = atoms(:,i) + vect1;
        o = o + 1;
        hydlist(:,o) = atoms(:,i) + vect2;
        o = o + 1;
    end
end
D.5. ZnO Nanowire/Bulk Creation

```
o = o - 1;
n = length(atoms);

disp(sprintf('Total number of atoms: %d', n + o));

if roughspecial == 0
    disp(sprintf('Boundaries: [0 0 0] - [%f %f %f]
                  a * numx, a * numy, a * numz));
else

    % Realign atoms prior to writing
    atoms(1,:) = atoms(1,:) + ucellx;
    atoms(2,:) = atoms(2,:) + ucelly;
    disp(sprintf('Boundaries: [%f %f %f] - [%f %f %f]
                  0, 0, 0, a * (numx + 2), a * (numy + 2),
                  a * numz));
end

% Write to file
fid = fopen(outp, 'w');
fprintf(fid, '%d

', n + o);
for i = 1:n
    fprintf(fid, '%s %f %f %f
', elem, atoms(1,i), atoms(2,i), atoms(3,i));
end
for i = 1:o
    fprintf(fid, '%s %f %f %f
', 'H', hydlist(1,i), hydlist(2,i), hydlist(3,i));
end
fclose(fid);
```

D.5 ZnO Nanowire/Bulk Creation

```
% Generate ZnO crystal lattice

clear all
close all

% Structmod 1 = Core
% Structmod 2 = Roughness
```
D.5. ZnO Nanowire/Bulk Creation

%Structmod 3 = Wurtzite/Zincblende (sphalerite) Mix (Polymorphic blend)
%Structmod 4 = Needles
%Structmod 5 = Nanovoid
%Structmod 6 = Track etched (synchotron)
%Structmod 7 = ZnO/Zn superlattice

%Parameters
a = 3.21; %Phonon
b = 3.30; %Phonon
charge = 0.0; %Ionic charge in eV
%a = 3.29; %Phonon - new after minimization
%c = 5.33; %Phonon - new after minimization
%charge = 2.0; %Ionic charge in eV
zb = 4.62; %Phonon
zi = 2.66; %Phonon
zic = 4.947; %Phonon
%a = 3.21; %Electron
%c = 5.1; %Electron

numx = 5; %Number of unit cells radius
numy = 5; %Number of unit cells radius
numz = 200; %Number of unit cells along z axis
makehex = true;

%Lattice vectors
a1 = [a 0 0];
a2 = [0.5*a sqrt(3)/2*a 0];
a3 = [0 0 c];

%Structural modification
structmod = 5;
%Structmod = 1: Core
corenumx = 7;
corenumy = 7;

%Structmod = 2: Roughness
roughperiod = 4*c; %Period of breaks in A
roughdepth = 1*a; %depth of ring
roughdia = 1*c; %Diameter/Length/Height of ring

%Structmod = 3: Polymorphic
polythickW = 2; %Wurtzite number of uc thick
polythickZB = 2; %Zincblende number of uc thick

%Structmod = 4: Needles
needleperiod = 4*c;
needleradius = 2;

%Structmod = 5: Nanovoids
voidradius = 5;
voidvariability = 50; %Percent randomness of radius
voiddensity = 40; %Percent coverage in the body
voidrng = 2;

%Structmod = 6: Track etched
holeradius = 5;
holevariability = 20; %Percent randomness of radius
holedensity = 20; %Percent coverage in the body
holeaxis = 'x'; %'x' is just x-axis, 'y' is just 'y' axis, 'xy' is a random angle along xy plane

%Structmod = 7: Superlattice
polythickZn0 = 2; %Wurtzite number of uc thick
polythickZn = 2; %Zincblende number of uc thick
celltype = 'Wurtzite';
elem1 = 'Zn';
elem2 = 'O';

if structmod == 3 || structmod == 7
    polyVec = [];
    if structmod == 3
        for i = 1:numz
            if mod(i - 1, polythickW + polythickZB) < polythickW
                polyVec(i) = 0;
            else
                polyVec(i) = 1;
            end
        end
    else
        for i = 1:numz
            if mod(i - 1, polythickZnO + polythickZn)
                < polythickZn0
                polyVec(i) = 0;
            else
                polyVec(i) = 2;
            end
        end
    end
end

if makehex == true
    numx = numx * 2 - 1;
else
    u = 1/3 * (a/c)^2 + 1/4;
    unitcellZn = [0 0 0; 0.5*a sqrt(3)/6*a c/2]';
    unitcellO = [0 0 u*c; 0.5*a sqrt(3)/6*a (u+0.5)*c]';

    supercell = [];
    m = 1;
    if makehex == true
        numx = numx * 2 - 1;
end
D.5. ZnO Nanowire/Bulk Creation

```plaintext
numy = numy * 2 - 1;
end
for k = 1:numz
  for i = 1:numx
    for j = 1:numy
      x = (i - 1) * a1(1) + (j - 1) * a2(1);
      y = (i - 1) * a1(2) + (j - 1) * a2(2);
      z = (k - 1) * a3(3);
      supercell(:,m) = [x y z];
      m = m + 1;
    end
  end
end
if makehex == true
  numx = (numx + 1) / 2;
  numy = (numy + 1) / 2;
end

% Assemble list of atoms
atomsZn = [];
atomsO = [];
nZn = 1;
nO = 1;
for i = 1:(m - 1)
  for j = 1:size(unitcellZn,2)
    uc = unitcellZn(:,j);
    x = supercell(1,i) + uc(1);
    y = supercell(2,i) + uc(2);
    z = supercell(3,i) + uc(3);
    atomsZn(:,nZn) = [x y z];
    nZn = nZn + 1;
  end
  for j = 1:size(unitcellO,2)
    uc = unitcellO(:,j);
    x = supercell(1,i) + uc(1);
    y = supercell(2,i) + uc(2);
    z = supercell(3,i) + uc(3);
    atomsO(:,nO) = [x y z];
    nO = nO + 1;
  end
end
```

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\texttt{n0 = n0 + 1;}

\texttt{end}

\texttt{end}

\texttt{if makehex == true}
  \texttt{\%And trim}
  \texttt{m = (a1(2) * numy - a2(2) * numy) / (a1(1) * numx - a2(1) * numx);}
  \texttt{b = a2(2) * (numy - 1) - m * a2(1) * (numx - 1);}
  \texttt{atomsZn(:,atomsZn(2,:)<(atomsZn(1,:)*m+b-a)) = [];
 atomsO(:,atomsO(2,:)<(atomsO(1,:)*m+b-a)) = [];
 b = (a2(2) + a1(2)) * (numy - 1) - m * (a2(1) + a1(1) * 2) * (numx - 1);
 atomsZn(:,atomsZn(2,:)>=(atomsZn(1,:)*m+b+1*a)) = [];
 atomsO(:,atomsO(2,:)>=(atomsO(1,:)*m+b+1*a)) = [];
}
\texttt{end}

\texttt{end}

\texttt{\%Round and delete duplicate atoms}
\texttt{\%atomsZn = round(atomsZn*100)/100;}
\texttt{\%atomsO = round(atomsO*100)/100;}
\texttt{\%atomsZn = unique(atomsZn', 'rows');}
\texttt{\%atomsO = unique(atomsO', 'rows');}

\texttt{\%Center}
\texttt{shiftx = mean(atomsZn(1,:),2);}
\texttt{shifty = mean(atomsZn(2,:),2);}
\texttt{atomsZn = atomsZn - [ones(1,length(atomsZn))*shiftx;
\hspace{1em}ones(1,length(atomsZn))*shifty;zeros(1,length(atomsZn))];}
\texttt{atomsO = atomsO - [ones(1,length(atomsO))*shiftx;
\hspace{1em}ones(1,length(atomsO))*shifty;zeros(1,length(atomsO))];}
D.5. ZnO Nanowire/Bulk Creation

%Structural modification 1 - hex core the structure
if structmod == 1
    rlim = a * corenumx;
    llim = -a * corenumx;
    tlim = 0.5 * a * corenumy;
    blim = -0.5 * a * corenumy;

    atomstmp = atomsZn;
    atomstmp(:,atomstmp(1,:).^2+atomstmp(2,:).^2<(0.5*a*corenumx).^2) = [];
    atomsZn = atomstmp;

    atomstmp = atomsO;
    atomstmp(:,atomstmp(1,:).^2+atomstmp(2,:).^2<(0.5*a*corenumx).^2) = [];
    atomsO = atomstmp;
end

%Roughen if required
if structmod == 2
    %Get diameter
    dia = max(atomsZn(1,:)) - min(atomsZn(1,:));
    rz = -roughperiod; %Include offset
    while rz < c * numz
        rz = rz + roughperiod;
        atomsZn(:,(atomsZn(1,:).^2+atomsZn(2,:).^2>((dia-roughdepth)/2)^2)&(atomsZn (3,:)>=rz)&(atomsZn(3,:)<=(rz+roughdia))) = [];
      atomsO(:,(atomsO(1,:).^2+atomsO(2,:).^2>((dia-roughdepth)/2)^2)&(atomsO(3,:)>=rz)&(atomsO(3,:)<=(rz+roughdia))) = [];
    end
end

%Structural modification 5 - Nanovoids
if structmod == 5
    %rng('default');
    rng(voidrng);
end
D.5. ZnO Nanowire/Bulk Creation

% Determine apprx volume of structure and voids
dia = max(atomsZn(1,:)) - min(atomsZn(1,:));
len = max(atomsZn(3,:)) - min(atomsZn(3,:));
volStruct = pi * (dia / 2) ^ 2 * len;
volVoid = 4 / 3 * pi * (voidradius) ^ 3;

numVoids = volStruct * voiddensity / 100 / volVoid;
disp(sprintf('Number of voids: %d', numVoids));

% Generate and implement voids
for i = 1:numVoids
    voidX = rand() * dia + min(atomsZn(1,:));
    voidY = rand() * dia + min(atomsZn(2,:));
    voidZ = rand() * len + min(atomsZn(3,:));
    voidR = (rand() * voidvariability / 100 - voidvariability / 200 + 1) * voidradius;
    atomsZn(:,((atomsZn(1,:)-voidX).^2+(atomsZn(2,:)-voidY).^2+(atomsZn(3,:)-voidZ).^2<=voidR^2)) = [];
end

% Structural modification 6 - Track etched
if structmod == 6
    rng('default');

    % Determine apprx volume of structure and voids
    dia = max(atomsZn(1,:)) - min(atomsZn(1,:));
    len = max(atomsZn(3,:)) - min(atomsZn(3,:));
    volStruct = pi * (dia / 2) ^ 2 * len;
    volHole = dia * pi * (holeradius) ^ 2;
    numHoles = volStruct * holedensity / 100 / volHole;
end
D.5. ZnO Nanowire/Bulk Creation

%Generate and implement voids
for i = 1:numHoles
    if holeaxis == 'x'
        holeY = rand() * dia + min(atomsZn(2,:))
        ;
        holeZ = rand() * len + min(atomsZn(3,:))
        ;
        holeR = (rand() * holevariability / 100
            - holevariability / 200 + 1) *
            holeradius;
        atomsZn(:,(atomsZn(2,:)-holeY).^2+(atomsZn(3,:)-holeZ).^2<=holeR^2) = [];
        atomsO(:,(atomsO(2,:)-holeY).^2+(atomsO(3,:)-holeZ).^2<=holeR^2) = [];
    end
    if holeaxis == 'y'
        holeX = rand() * dia + min(atomsZn(1,:))
        ;
        holeZ = rand() * len + min(atomsZn(3,:))
        ;
        holeR = (rand() * holevariability / 100
            - holevariability / 200 + 1) *
            holeradius;
        atomsZn(:,(atomsZn(1,:)-holeX).^2+(atomsZn(3,:)-holeZ).^2<=holeR^2) = [];
        atomsO(:,(atomsO(1,:)-holeX).^2+(atomsO(3,:)-holeZ).^2<=holeR^2) = [];
    end
    if holeaxis == 'xy'
        holeX = rand() * dia + min(atomsZn(1,:))
        ;
        holeZ = rand() * len + min(atomsZn(3,:))
        ;
        holeR = (rand() * holevariability / 100
            - holevariability / 200 + 1) *
            holeradius;
        atomsZn(:,(atomsZn(1,:)-holeX).^2+(atomsZn(3,:)-holeZ).^2<=holeR^2) = [];
        atomsO(:,(atomsO(1,:)-holeX).^2+(atomsO(3,:)-holeZ).^2<=holeR^2) = [];
    end

%TODO
D.5. ZnO Nanowire/Bulk Creation

```matlab
holeradius;
atomsZn(:,(atomsZn(1,:)-holeX).^2+(atomsZn(3,:)-holeZ).^2<=holeR^2) = [];
atomsO(:,(atomsO(1,:)-holeX).^2+(atomsO(3,:)-holeZ).^2<=holeR^2) = [];

end
end
end

nZn = size(atomsZn, 2);
disp(sprintf('Total number of Zn atoms: %d', nZn));
nO = size(atomsO, 2);
disp(sprintf('Total number of O atoms: %d', nO));
if ~exist('zTotal')
zTotal = numz * c;
end

%Shift for bulk
if makehex == false
    shiftx = min(atomsZn(1,:));
    shifty = min(atomsZn(2,:));
atomsZn = atomsZn - [ones(1,length(atomsZn))*shiftx;ones(1,length(atomsZn))*shifty;zeros(1,length(atomsZn))];
atomsO = atomsO - [ones(1,length(atomsO))*shiftx;ones(1,length(atomsO))*shifty;zeros(1,length(atomsO))];
end

%Write to file
fid = fopen(outp, 'w');
if fout == 0  %xyz format
    fprintf(fid, '%d\r\n\r\n', nZn + nO);
    for i = 1:nZn
        fprintf(fid, '%s %f %f %f\r\n', elem1, atomsZn(1,i), atomsZn(2,i), atomsZn(3,i))
    end
```
D.5. ZnO Nanowire/Bulk Creation

```matlab
for i = 1:nO
    fprintf(fid, '%s %f %f %f\r\n', elem2,
            atomsO(1,i), atomsO(2,i), atomsO(3,i));
end
else
    if fout == 1 %SIESTA compatible format
        tcount = 1;
        for i = 1:nZn
            fprintf (fid, '\t%f\t%f\t%f\n', atomsZn(1,i), atomsZn(2,i),
                      atomsZn(3,i), tcount);
            tcount = tcount + 1;
        end
        for i = 1:nO
            fprintf (fid, '\t%f\t%f\t%f\n', atomsO(1,i), atomsO(2,i), atomsO(3,i), tcount);
            tcount = tcount + 1;
        end
    else
        if fout == 2 %LAMMPS compatible format
            fprintf (fid, 'LAMMPS data file\r
            %d atoms\n', nZn + nO);
            fprintf (fid, ' 0 bonds\n');
            fprintf (fid, ' 0 angles\n');
            fprintf (fid, ' 0 dihedrals\n');
            fprintf (fid, ' 0 impropers\n');
            fprintf (fid, ' 2 atom types\n');
            fprintf (fid, ' 0 bond types\n');
            fprintf (fid, ' 0 angle types\n');
            fprintf (fid, ' 0 dihedral types\n');
            fprintf (fid, ' 0 improper types\n');
            if makehex == true
                fprintf (fid, ' -50.0 50.0 xlo xhi\n
');
                fprintf (fid, ' -50.0 50.0 ylo yhi\n
');
                fprintf (fid, ' 0.000 %.2f zlo zhi\n\n', zTotal);
            else
```

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D.6. Generate LDOS-EMD LAMMPS Script for Void Structures

```matlab
fprintf(fid, ' -0.01 %.2f xlo xhi
  n', numx * a);
fprintf(fid, ' -0.01 %.2f ylo yhi
  n', numy * a * sqrt(3) / 2);
fprintf(fid, ' -0.01 %.2f zlo zhi
  n', zTotal);
fprintf(fid, ' %.3f 0.00 0.00 xy xz
  yz\r\n\n', numx * a / 2);
end
fprintf(fid, ' Masses\n
  1 15.999400
  2 65.408997\r\n\n Atoms\n
  ', tcount = 1;
for i = 1:nZn
  fprintf(fid, '%d %d %f %f %f %f\r\n',
    tcount, 2, charge, atomsZn(1,i)
    , atomsZn(2,i), atomsZn(3,i));
  tcount = tcount + 1;
end
for i = 1:nO
  fprintf(fid, '%d %d %f %f %f %f\r\n',
    tcount, 1, -charge, atomsO(1,i)
    , atomsO(2,i), atomsO(3,i));
  tcount = tcount + 1;
end
end
disp(sprintf('Boundaries: [%f %f 0] - [%f %f %f]',
  min(atomsZn(1,:)), min(atomsZn(2,:)),
  max(atomsZn(1,:)), max(atomsZn(2,:)), zTotal));
fclose(fid);
```

D.6 Generate LDOS-EMD LAMMPS Script for Void Structures

%Build in.ZnOmp for a LAMMPS simulation of
D.6. Generate LDOS-EMD LAMMPS Script for Void Structures

progressively voiding ZnO NW using LDOS-EMD

clear all
close all

fnameOut = 'inR8.ZnOmp';
fnameStruct = 'ZnOstraightHex5x5x200.lammps';

voidvariability = 50;  %Percent randomness of radius
voiddensity = 50;     %Percent coverage in the body

%voidradius = 3;
%voidgrowthrate = 200;  %#/voids per simulation batch - R3
%voidrng = 1;
voidradius = 8;
voidgrowthrate = 10;  %#/voids per simulation batch - R5
voidrng = 8;

%Grab data from structure file
structData = importdata(fnameStruct, ' ', 22);
minx = min(structData.data(:,4));
maxx = max(structData.data(:,4));
miny = min(structData.data(:,5));
maxy = max(structData.data(:,5));
minz = min(structData.data(:,6));
maxz = max(structData.data(:,6));

%Generate total pattern of nanovoids
rng(voidrng);

%Determine apprx volume of structure and voids
dia = maxx - minx;
len = maxz - minz;
volStruct = pi * (dia / 2) ^ 2 * len;
volVoid = 4 / 3 * pi * (voidradius) ^ 3;
D.6. Generate LDOS-EMD LAMMPS Script for Void Structures

$numVoids = \text{volStruct} * \text{voiddensity} / 100 / \text{volVoid};$

%%%Generate voids
for $i = 1 : numVoids$
    voidX($i$) = rand() * dia + minx;
    voidY($i$) = rand() * dia + miny;
    voidZ($i$) = rand() * len + minz;
    voidR($i$) = ( rand() * voidvariability / 100 -
                    voidvariability / 200 + 1) * voidradius;
end

%%%Build output file
fp = fopen(fnameOut, 'w');
%preamble...
fprintf(fp, 'units	real
boundary	s s p
echo	both
newton	ton

');
fprintf(fp, 'atom_style	charge
read_data	%s

' , fnameStruct);
fprintf(fp, 'pair_style	reax/c NULL
pair_coeff	* * ffield.reax O Zn

');
fprintf(fp, 'timestep	0.5
neighbor	2.0 bin
nneigh_modify	every 20 delay 0 check no

');
fprintf(fp, 'velocity	all create 300 2347623 dist
fix	1 all npt temp 300.0 300.0 500.0
fix	2 all qeq/reax 1 0.0 10.0 reax/c

');
fprintf(fp, 'run	100000
unfix 1

');
fprintf(fp, 'fix	3 all nve
fix	7 all temp/berendsen 300.0 300.0 20000.0
run	50000
undump t1

');
fprintf(fp, 'dump	1 all custom 40 dumpforce40 -0.
ZnO id type mass x y z vx vy vz fx fy fz
ndump_modify	1 sort id
run	50000
undump t1

');
indVoids = 1;
ind = 1;
groupind = 1;
while indVoids < numVoids
D.7. Generate VAF Slices for Simple LDOS-EMD

%Add voids
for i = 1:voidgrowthrate
    fprintf(fp, 'region\t\treg%d sphere %.5f %.5f %.5f side in\ndelete_atoms\t\tregion
        reg%d compress no\n', ind, voidX(ind), voidY(ind), voidZ(ind), voidR(ind), ind);
    ind = indVoids + i;
    if ind >= numVoids
        break;
    end
end
indVoids = indVoids + voidgrowthrate;

%Stabilize and run simulation
fprintf(fp, '\nrun\t\t100000\n
');
fprintf(fp, 'dump\t\t1 all custom 40 dumpforce40
        -%d.ZnO id type mass x y z vx vy vz fx fy fz\n        ndump_modify\t\t1 sort id\nnrun\t\t150000\nundump
        \t\t1\n\n', indVoids);
    groupind = groupind + 1;
end
fclose(fp);

disp(sprintf('Complete. %d groups of 150,000 simulation steps created.', groupind));

% Go through various materials and compare VAF-based calc to simulated thermal properties

clear all
close all
if matlabpool('size') == 0
    matlabpool
end

%ZNO DATA
D.7. Generate VAF Slices for Simple LDOS-EMD

```matlab
fnameOut = 'vafZnOVoidScanR8.mat';
timeFactor = 0.5e-15;
numSlices = 400; % For full structure

fnames = {'ZnOvoidLDOSR8-0', 'ZnOvoidLDOSR8-11', 'ZnOvoidLDOSR8-21', 'ZnOvoidLDOSR8-31', 'ZnOvoidLDOSR8-41', 'ZnOvoidLDOSR8-51', 'ZnOvoidLDOSR8-61', 'ZnOvoidLDOSR8-71', 'ZnOvoidLDOSR8-81', 'ZnOvoidLDOSR8-91', 'ZnOvoidLDOSR8-101', 'ZnOvoidLDOSR8-111'};
calcThermal = [4.4 0 0 0 0 0 0 0 0 0 0 0];
calcTemp = [300 300 300 300 300 300 300 300 300 300 300 300];

% SI DATA

fnameOut = 'vafSiBulk5x4x400.mat';
timeFactor = 1e-15;
numSlices = 200;

% New data, full mp

fnames = {'Sistraight3x3x400', 'Sistraight4x4x400', 'Sistraight5x5x400', 'Sistraight6x6x400', 'Sistema7x7x400', 'Sistema8x8x400', 'Sistema9x9x400', 'SiP10aD1aW1a9x9x400', 'SiP10aD2aW1a9x9x400', 'SiP10aD3aW1a9x9x400', 'SiP10aD4aW1a9x9x400', 'SiP2aD1aW1a5x5x400', 'SiP10aD1aW1a7x7x400', 'SiP10aD1aW2a7x7x400', 'SiP10aD1aW3a7x7x400', 'SiP10aD1aW4a7x7x400', 'SiP10aD1aW5a7x7x400', 'SiP10aD1aW6a7x7x400', 'SiP10aD1aW7a7x7x400', 'SiP10aD1aW8a7x7x400', 'SiP10aD1aW9a7x7x400'};
 calcTemp = [300 300 300 300 300 300 300 300 300 300 300 300];
```
D.7. Generate VAF Slices for Simple LDOS-EMD

```matlab
% Prepare data set
for k = 1:length(fnames)
    % Prepare variables and load data
    vafz = [];
    dos = [];
    dosn = [];
    datavz = [];
    dataz = [];
    disp(sprintf('Doing %s', fnames{k}));
    % New method
    indata = load(sprintf('%s.dat', fnames{k}));
    tmp = unique(indata(:,1));  % Group by timestamp
    for i = 1:length(tmp)
        dataz(:,i) = indata(indata(:,1)==tmp(i),6);
        datavz(:,i) = indata(indata(:,1)==tmp(i),9);
    end
    timeperstep = (tmp(2) - tmp(1)) * timeFactor;
    clear indata;
    clear a;
    clear b;
    tindex = 1;
    parfor i = 1:length(datavz(:,tindex))
        vafz(i,:) = fft(full(datavz(i,:)));  
    end
    vafz = vafz .* conj(vafz);
    vafz = abs(vafz);
    vafz = vafz(:,1:(size(vafz,2)-1)/2);
    freqs = linspace(0, 1 / timeperstep / 2, size(
```
D.7. Generate VAF Slices for Simple LDOS-EMD

```matlab
vafz, 2));

% Chop up into slices
% tslice = dataz(dataz(:,tindex)>135.75&dataz(:,
tindex)<950.25,tindex);
tslice = dataz(:,tindex);
slices = full(linspace(min(tslice), max(tslice),
numSlices));
smin = min(slices);
dos = [];
for i = 1:(length(slices)-2) %-6
    ai = find((dataz(:,tindex)>slices(i))&(dataz(:,tindex)<(slices(i+1)))); %Build
    index of slice, Angstroms, %+5
    natoms(i) = length(ai);
dos(:,i) = sum(vafz(ai,:)); %Inefficient , but works
dosn(:,i) = sum(vafz(ai,:)) ./ natoms(i);
end

dosOut = dos;
freqsOut = freqs;
%
%{ xin = linspace(1, 625, size(dos, 1));
xout = 1:625;
dosOut = interp1(xin, dos, xout);
freqsOut = interp1(xin, freqs, xout);%
}%
%
% Remove bad points - ZnO
%dosOut(dosOut>30) = 0;

calcVAF(:,:,k) = sum(sum(vafz)); %Different
sizes each
calcDOS(:,:,k) = dosOut;

x = 1:size(dosOut, 2);
y = freqsOut / 1e12;
figure('Color', [1 1 1]);
```
D.8 Generate VAF Slices for Advanced LDOS-EMD

```matlab
%Go through various materials and compare VAF-based calc to simulated thermal properties

close all
if matlabpool('size') == 0
    matlabpool
end
chdir('/data/phonon');
if donew
    timeFactor = 0.5e-15;
    %Prep
    chdir('/data/phonon');
    %Prepare data set
    for k = 1:1
        %Prepare variables and load data
        vafz = [];
```
D.8. Generate VAF Slices for Advanced LDOS-EMD

dos = []; dosn = []; datavz = []; datax = []; datay = []; dataz = [];

disp(sprintf('Doing %s', fname));

% New method
% Time index to collect spatial information

% For each unique timestamp group, collect data
% Group by timestamp

datax(:,i) = indata(indata(:,1)==tmp(i),4);
datay(:,i) = indata(indata(:,1)==tmp(i),5);
dataz(:,i) = indata(indata(:,1)==tmp(i),6);

datavz(:,i) = indata(indata(:,1)==tmp(i),9);

end

timeperstep = (tmp(2) - tmp(1)) * timeFactor;
clear indata;
clear a;
clear b;

parfor i = 1:length(datavz(:,tindex))
    vafz(i,:) = fft(full(datavz(i,:)));
end
vafz = vafz .* conj(vafz);
vafz = abs(vafz);
D.8. Generate VAF Slices for Advanced LDOS-EMD

```matlab
vafz = vafz(:,1:(size(vafz,2)-1)/2);
freqs = linspace(0, 1 / timeperstep / 2, size(vafz, 2));
end
end

%%Grab subsections and calculate thermal conductivity
chunkDiv = 4;
chunkDensity = 50;
numSlices = 50;

%Clean up
cc = find((datax(:,1)>30) | (datax(:,1)<-30) | (datay(:,1)>30) | (datay(:,1)<-30) | (dataz(:,1)>2000) | (dataz(:,1)<-5));
datax(cc,:) = [];
datay(cc,:) = [];
dataz(cc,:) = [];
datavz(cc,:) = [];

%Determine size and atom density
xmin = min(datax(:,1));
xmax = max(datax(:,1));
ymin = min(datay(:,1));
ymax = max(datay(:,1));
zmin = min(dataz(:,1));
zmax = max(dataz(:,1));
vol = (xmax - xmin) * (ymax - ymin) * (zmax - zmin);
numAtoms = size(vafz,1);

%Size of chunks
%xsize = (xmax - xmin) / 4;
%ysize = (ymax - ymin) / 4;
%zsize = chunkDensity / (numAtoms / vol) / xsize / ysize;
xsize = 10;
ysize = 10;
zsize = (zmax - zmin) / 400;
```
D.8. Generate VAF Slices for Advanced LDOS-EMD

\begin{verbatim}
disp(sprintf('x-size: %.3f A, y-size: %.3f A, z-size : %.3f A', xsize, ysize, zsize));
tcondmatrix = zeros(350,8);

%Main loop
parfor nn = 1:8
  rng('shuffle');
  s = rng();
  rng(s.Seed + nn);  %video
  natoms = [];
  kVector = [];
  mfpMatrix = [];
  mm = 1;
  xpos = xmin + xsize + rand () * (xmax - xmin - 2 * xsize);
  ypos = ymin + ysize + rand () * (ymax - ymin - 2 * ysize);
  disp (sprintf('Starting %d', nn));
  for i = 1:350
    zpos = zmin + i * zsize;
    dos = [];
    for j = 1:numSlices
      zstart = (zpos + zsize * (j - 1));
      zstop = (zpos + zsize * (j + 1));
      if(zstart > zmax)  %Clean up - boundary case
        zstart = zstart - zmax;
      end
      ai = find ( (datax(:,1)>xpos) & (datax(:,1)<(xpos+xsize)) & (datay(:,1)>ypos) & (datay(:,1)<(ypos+ysize)) & (dataz(:,1)>zstart) & (dataz(:,1)<zstop) );
      natoms(j,i) = length(ai);
      if length(ai) < 2
        continue
      end
  end

end

\end{verbatim}
end

dos(:,j) = sum(vafz(ai,:));  \%
Inefficient, but works
end

end

%natoms(:,i)'

dosOut = dos;

if size(dosOut,2) < numSlices - 10
    kVector(mm) = 0;
    mm = mm + 1;
    continue
end

%Determine thermal conductivity

kcalc = 0;
tmp = [];
P = [];
tmp3 = [];

freqs = linspace(0, 25e12, size(dosOut,1));
distance = zmax - zmin;  \%
    Angstroms of material examined along z-axis
a = zsize;  \%Length of each slice
kB = 1.3806488e-23;
hbar = 1.05457173e-34;
T = 300;

%Run MFP calculation on a single offset
for j = 2:size(dosOut,1)  \%Each frequency band except DC
    vec = dosOut(j,:);  \%Grab subset of slice data for analysis
    mfp = 0;
P(1) = 0;
    \%Calculate MFP
    for k = 2:length(vec)
        if max([vec(k) vec(k-1)]) == 0
            mfp = 0;
            P(1) = 0;
        end
    end
end
D.8. Generate VAF Slices for Advanced LDOS-EMD

\[
P(k) = 1; \quad \text{Probability of collision}
\]

\[
\text{else}
\]

\[
P(k) = 1 - \frac{\text{abs}(\text{vec}(k) - \text{vec}(k-1))}{\max([\text{vec}(k) \text{ vec}(k-1)])};
\]

\[
\text{end}
\]

\[
\text{end}
\]

\[
\text{for } k = 2: \text{length(vec)}
\]

\[
mfp = mfp + (k - 1) \ast a \ast \prod(P(2:k)) \ast (1 - P(k));
\]

\[
\text{end}
\]

\[
\% Special cases
\]

\[
tmp(j) = mfp;
\]

\[
\text{if}(P(2) == 1) \quad \% \text{No atoms at beginning of structure}
\]

\[
\text{continue;}
\]

\[
\text{end}
\]

\[
\% Calculate other requirements
\]

\[
dos = \text{vec}(1);
\]

\[
x = \hbar \ast 2 \ast \pi \ast \text{freqs}(j) / k\text{B} / T;
\]

\[
\text{char} = k\text{B} \ast x ^ 2 \ast \exp(x) / ((\exp(x) - 1) ^ 2);
\]

\[
\text{kcalc} = \text{kcalc} + \text{char} \ast mfp \ast dos \ast (\text{freqs}(2) - \text{freqs}(1)); \% \ast dos;
\]

\[
\text{end}
\]

\[
\% \text{mfpMatrix(:,mm)} = \text{tmp};
\]

\[
\text{kVector(mm)} = \text{kcalc};
\]

\[
\text{mm} = \text{mm} + 1;
\]

\[
\text{end}
\]

\[
\text{tcondmatrix(:,nn)} = \text{kVector};
\]

\[
\text{thermalCond(nn)} = 1 / \text{sum}(1 ./ \text{kVector}) \ast (\text{mm} - 1);
\]

\[
\text{xp(nn)} = \text{xpos};
\]

\[
\text{yp(nn)} = \text{ypos};
\]

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D.9 Thermal Conductivity Using Simple LDOS-EMD

Approximate thermal conductivity from phonon information. Requires data file generated using vafcalc.m.

clear all
close all

Load data
chdir('~/data/phonon');
load vafZnOVoidScan

% Data setup – TODO: automate some of the constants
freqs = linspace(0, 25e12, 1250);
distance = 814.5; % Angstroms of material examined along z-axis
a = distance / size(calcDOS, 2); % Length of each slice
kB = 1.3806488e-23;
hbar = 1.05457173e-34;
T = 300;

% Go through data and calculate thermal conductivities based on phonons
kcalc = [];
if 1 == 1
    mfp = [];
    for i = 1:size(calcDOS, 3) % Each structure
        kcalc(i) = 0;
        for j = 2:size(calcDOS, 1) % Each frequency band except DC
            vec = calcDOS(j, 10:end-10, i); % Remove unfilled slices from beginning/end
            mfp = 0;
            % Calculate MFP
            for k = 2:length(vec)
                P(k) = 1 - abs(vec(k) - vec(k-1)) / max([vec(k) vec(k-1)]);
            end
            for k = 2:length(vec)
                mfp = mfp + (k - 1) * a * prod(P(2:(k-1))) * (1 - P(k));
            end
        end
    end
end

dos = sum(vec); % TODO - normalize by cross-sectional area or something similar?
x = hbar * 2 * pi * freqs(j) / kB / T;
char = kB * x ^ 2 * exp(x) / ((exp(x) - ...
1) \sim 2);  
kcalc(i) = kcalc(i) + (freqs(2) - freqs(1)) * char * dos * mfp;  
end  
tmp(j) = mfp;  
end  
fprintf('MFP %s: %.2f
', calcNames{i}, mfp)  
end  
end  
if 1 == 0  
for i = 1:size(calcDOS, 3) %Each structure  
variance = var(calcDOS(:,:,i), 0, 2);  
kcalc(i) = calcVAF(:,:,i) / sum(variance(2:end) ./ freqs(2:end')) / 1e12;  
end  
end  
normalizeOn = 1;  
figure('Color', [1 1 1]);  
h1 = plot(kcalc/kcalc(normalizeOn), 'b.-');  
hold on  
h2 = plot(calcThermal/calcThermal(normalizeOn), 'ro-');  
errorbar(calcThermal/calcThermal(normalizeOn), linspace(0.2/calcThermal(normalizeOn), 0.2/calcThermal(normalizeOn)), 'ro');  
set(gca, 'fontsize', 15);  
text(1:length(kcalc), kcalc/kcalc(normalizeOn), calcNames);  
xlabel('Nanowire Structure');  
ylabel('NEMD Thermal Conductivity (W/mK)');  

%Additional plotting of Advanced LDOS data for comparison (optional)  
load thermalLDOS1Results10  
newy = [];  
for i = 1:length(simResult)
D.10 Thermoelectric Calibration and Analysis

```matlab
x = find(strcmp(simName{i}, calcNames));
newy(end+1,x) = simResult(i);
end
newy(isnan(newy)) = 0;
for i = 1:size(newy, 2)
    newyy(i) = median(newy(newy(:,i)~=0,i));
    newye(i) = std(newy(newy(:,i)~=0,i));
end
yscale = newyy(normalizeOn);
for i = 1:size(newy, 2)
    plot(i, newy(newy(:,i)~=0,i) / yscale, 'gx', 'markersize', 10);
end
h3 = plot(newyy / yscale, 'g');
errorbar(newyy / yscale, newye / yscale, 'go');
legend([h1 h2 h3], {'LDOS-EMD', 'NEMD', 'LDOS-EMD-Seg'});

D.10 Thermoelectric Calibration and Analysis

%parsedata.m - Parse experimental data and produce plots

clear all
close all
indexList = [];
fnames = [];
names = [];
areaList = [];
thicknessList = [];
genComp = false;
doRadiance = false;
newApparatus = false;
calNameHigh = [];
```
D.10. Thermoelectric Calibration and Analysis

calNameLow = [];
doConductivity = true;

%Calibrations
calNameLow = 'TE402ContactCal2'; calIndexLow = round (3600 * [0.4128 0.8508 1.9 2.342 2.941 3.168]);
calAreaLow = pi * 0.0125 ^ 2;

fnames{ end +1} = 'TE402ContactCal2'; names{ end +1} = 'Closed Cal 1'; indexList(1:6, end +1) = round (3600 * [0.8508 1.297 1.9 2.342 2.97 3.168]); areaList( end +1) = pi * 0.0125 ^ 2; thicknessList(end+1) = 1e-6;

fnames{ end +1} = 'TE405OpenCal'; names{ end +1} = 'Open Cal 1'; indexList(1:7, end +1) = round (3600 * [0.3714 0.8544 1.307 1.822 2.435 2.731 3.403]); areaList(end+1) = 1.487e-3; thicknessList(end+1) = 0.02; doRadiance = true;

fnames{ end +1} = 'TE401nTypeTest'; names{ end +1} = 'n-type Si'; indexList(1:6, end +1) = round (3600 * [0.03444 0.1847 0.3775 0.7172 0.8897 1.081]); areaList(end+1) = 75.3e-6; thicknessList(end+1) = 500e-6; 0.001 Ohm-cm

colour = varycolor(length(fnames));

len = length(fnames);

for i = 1:len
  f = sprintf('..../Experimental/%s.csv', fnames{i});
  dat = load(f);
  if ~isempty(indexList)
    indeces = indexList(:,i);
    indeces(indeces==0) = [];
  else
    
end
indeces = [];
end
if ~isempty(areaList)
    area = areaList(i);
else
    area = [];
end
if ~isempty(thicknessList)
    thickness = thicknessList(i);
else
    thickness = [];
end
datTime = dat(:,1);
heaterVoltage = dat(:,2);
heaterPower = dat(:,3);
tempProbe = dat(:,4);
tempPlate = dat(:,7);
elecPower = dat(:,8);
elecResistance = dat(:,9);
elecVoltage = dat(:,10);
Z = dat(:,11);
ZT = dat(:,12);

%Apply calibration?
if ~isempty(calNameLow)

%Constants
Rloss = 2.2;  %Ohms of loss going to the heater
Rdratio = 0.63;  %Ratio of element to contact material series resistance - n-type
%Rdratio = 0.628;  %Ratio of element to contact material series resistance - n-type
%Rdratio = 0.52;  %Ratio of element to contact material series resistance - p-type
D.10. Thermoelectric Calibration and Analysis

```matlab
%Load cal data Low (direct contact)
calf = sprintf('../../Experimental/%s.csv', calNameLow);
calDat = load(calf);
calHeaterVoltageLow = calDat(calIndexLow,2);
calPowerLow = calDat(calIndexLow,3);
calTempProbeLow = calDat(calIndexLow,4);
calTempPlateLow = calDat(calIndexLow,7);
calElecPowerLow = calDat(calIndexLow,8);
calElecResistanceLow = calDat(calIndexLow,9);
calElecVoltageLow = -calDat(calIndexLow,10);

%Load cal data High (vacuum)
calf = sprintf('../../Experimental/%s.csv', calNameHigh);
calDat = load(calf);
calHeaterVoltageHigh = calDat(calIndexHigh,2);
calPowerHigh = calDat(calIndexHigh,3);
calTempProbeHigh = calDat(calIndexHigh,4);
calTempPlateHigh = calDat(calIndexHigh,7);
calElecPowerHigh = calDat(calIndexHigh,8);

%Adjust power measurements for calibration data
calPowerLow = calPowerLow - Rloss * (calPowerLow ./ calHeaterVoltageLow).^2;
calPowerHigh = calPowerHigh - Rloss * (calPowerHigh ./ calHeaterVoltageHigh).^2;

%Calculate Rb - losses due to radiative dissipation
%4th order fit for Stefan-Boltzmann law
tempDeltaHigh = calTempProbeHigh - calTempPlateHigh; %Plate serves as room temperature here
Rb = polyfit(tempDeltaHigh, calPowerHigh, 4);
```
%Calculate Rd - Native thermal resistance of electrode assembly
%1st order fit for thermal junction resistance
tempDeltaLow = calTempProbeLow - calTempPlateLow;
a = polyfit(calPowerLow, tempDeltaLow, 1);
Rd = a(1);

%Calculate Rc - Cable resistance error for power/resistance measurements
a = polyfit(calTempPlateLow, calElecResistanceLow, 1); %TODO - really temperature dependant?
Rc = a;

%Calculate Ve - Voltage from heater elements /etc assembly
Ve = polyfit(((calTempPlateLow + calTempProbeLow) / 2, calElecVoltageLow, 1);

%Adjust compensation for area changes
Rbnew = Rb * (2 * calAreaHigh - area) / (2 * calAreaHigh);  %x2 multiplier to include both top and bottom of electrode
Rdnew = Rd * Rdratio + Rd * (1 - Rdratio) * calAreaLow / area;  %TODO - tricky!! Only partially dependant on cross-sectional area

%Compensate for resistive losses on heater wiring
heaterPower = heaterPower - Rloss * (heaterPower ./ heaterVoltage) .^ 2;

%Adjust upper temperature for losses in radiation and electrode
Pdut = heaterPower - polyval(Rbnew,
D.10. Thermoelectric Calibration and Analysis

```matlab
tempProbe = tempPlate; % Radiative losses

Pdut = max(Pdut, 0);

if ~newApparatus
    elecResistance = elecResistance - Rc(1) * tempPlate - Rc(2);
    elecResistance(elecResistance < 0.01) = 0.001;
    elecVoltage = elecVoltage - polyval(Ve, (tempProbe + tempPlate) / 2);
end

% Adjust electrical measurements accordingly

tempDelta = tempProbe - tempPlate;
datTime = datTime - min(datTime); % Normalize to 0

elecVoltage = -elecVoltage; % Compensate for error in experimental setup

% Temperatures over time
if ~exist('f1')
    figure('Color', [1 1 1]);
else
    figure(f1);
    hold on
end
set(gca, 'fontsize', 15);
plot(datTime / 3600, tempProbe, 'r', 'linewidth', 2.0, 'Color', colour(i,:));
hold on;
plot(datTime / 3600, tempPlate, 'b', 'linewidth', 2.0, 'Color', colour(i,:));
if ~isempty(indeces)
    plot(datTime(indeces) / 3600, tempProbe(indeces), 'kx', 'markersize', 10, 'Color',
```
D.10. Thermoelectric Calibration and Analysis

, colour(i,:));
end
xlabel('Time (h)');
ylabel('Temperature (degC)');

%Temperature gradient over time
if ~exist('f2')
f2 = figure('Color', [1 1 1]);
else
    figure(f2);
    hold on
end
set(gca, 'fontsize', 15);
plot(datTime / 3600, tempDelta, 'linewidth', 2.0, 'Color', colour(i,:));
hold on;
if ~isempty(indeces)
    plot(datTime(indeces) / 3600, tempDelta(indeces), 'kx', 'markersize', 10, 'Color',
         colour(i,:));
end
xlabel('Time (h)');
ylabel('Temperature Difference (K)');

%%Analysis
if ~isempty(indeces)
    %Produce averages at index points
    for k = 1:length(indeces)
        heaterVoltage(indeces(k)) = mean(
            heaterVoltage((indeces(k)-10):(indeces(k)+10)));
        heaterPower(indeces(k)) = mean(
            heaterPower((indeces(k)-10):(indeces(k)+10)));
        tempProbe(indeces(k)) = mean(
            tempProbe((indeces(k)-10):(indeces(k)+10)));
        tempPlate(indeces(k)) = mean(
            tempPlate((indeces(k)-10):(indeces(k)+10)));
        tempDelta(indeces(k)) = mean(
            tempDelta((indeces(k)-10):(indeces(k)+10)));
    end
D.10. Thermoelectric Calibration and Analysis

\[ \text{elecPower(\text{indeces}(k))} = \text{mean(} \text{elecPower((indeces}(k)-10):(indeces(k)+10))) \]

\[ \text{elecResistance(\text{indeces}(k))} = \text{mean(} \text{elecResistance((indeces}(k)-10):(indeces(k)+10))) \]

\[ \text{elecVoltage(\text{indeces}(k))} = \text{mean(} \text{elecVoltage((indeces}(k)-10):(indeces(k)+10))) \]

\[ \text{a} = \text{polyfit(} \text{tempDelta(indeces)}, \text{heaterPower(indeces)}, 1); \]

\[ \text{b} = \text{polyval(a, tempDelta(indeces));} \]

\[ \text{Tcond} = a(1); \]

\[ \text{if } \text{ exist('f3')} \]
\[ \text{f3} = \text{figure('Color', [1 1 1]);} \]
\[ \text{else} \]
\[ \text{figure(f3);} \]
\[ \text{hold on} \]
\[ \text{end} \]

\[ \text{set(gca, 'fontsize', 15);} \]
\[ \text{plot(} \text{heaterPower(indeces)}, \text{tempDelta(indeces)}, '-x', 'markersize', 10, 'linewidth', 2.0, 'Color', colour(i,:)); \]
\[ \text{hold on;} \]
\[ \text{plot(b, tempDelta(indeces), 'k');} \]
\[ \text{xlabel('Thermal Power (W)');} \]
\[ \text{ylabel('Temperature Difference (K)');} \]

\[ \text{if doRadiance} \]
\[ \text{rad} = \text{heaterPower(indeces) ./ ( ( tempProbe(indeces) + 273.15)^4 - ( tempPlate(indeces) + 273.15)^4) / 5.67e-8;} \]
\[ \text{radConstant} = \text{mean(rad((end-4):end));} \]
\[ \text{radConstant} = \text{mean(rad(1:end));} \]
\[ \text{radConstant} = 0.0014; \]
D.10. Thermoelectric Calibration and Analysis

% Thermoelectric Calibration and Analysis

```matlab
yRad = ((tempPlate(induces) + 273.15) .^ 4 + heaterPower(induces) / radConstant / 5.67e-8 .^ (1/4) - 273.15 - tempPlate(induces);
plot(heaterPower(induces), yRad, 'k--');
disp(sprintf('Calculated emissivity: %f ', radConstant / areaList(i) / 2));
end

disp(sprintf('%s: Thermal conductance = %.3f W/K (conductivity = %.3f W/mK)', names{i}, Tcond, Tcond * thickness / area));

% Electrical conductance vs. thermal power
elecConductance = 1 ./ elecResistance;
if ~exist('f4')
f4 = figure('Color', [1 1 1]);
else
    figure(f4);
    hold on
end
set(gca, 'fontsize', 15);
plot(((tempProbe(induces) + tempPlate(induces)) / 2, elecConductance(induces), '-x', 'markersize', 10, 'linewidht', 2.0, 'Color', colour(i,:));
hold on;
xlabel('Average Temperature (degC)');
ylabel('Electrical Conductance (S)');
disp(sprintf('%s: Mean Electrical conductance = %.3f S (resistivity = %.3f Ohms-cm)', names{i}, mean(elecConductance(induces)), 1 / mean(elecConductance(induces)) * area / thickness * 100));

% Voltage vs. temperature Gradient
a = polyfit(tempDelta(induces), elecVoltage(induces), 1);
b = polyval(a, tempDelta(induces));
Seebeck = a(1) + 3.5e-6;  % Adjust for
```

% Electrical conductance vs. thermal power

% Voltage vs. temperature Gradient

```matlab
```
Aluminum so vs. Platinum

if ~exist('f5')
    f5 = figure('Color', [1 1 1]);
else
    figure(f5);
    hold on
end
set(gca, 'fontsize', 15);
plot(tempDelta(indeces), elecVoltage(indeces), '-x', 'markersize', 10, 'linewidth', 2.0, 'Color', colour(i,:));
hold on;
%plot(tempDelta(indeces), b, 'k');
xlabel('Temperature Difference (K)');
ylabel('Induced Voltage (V)');
disp(sprintf('%s: Seebeck Coefficient = %.3f \mu V/K', names{i}, Seebeck * 1e6));

%Calculate ZT
Zcalc = Seebeck ^ 2 * elecConductance ./ Tcond; %TODO - Tcond(T)?
Tavg = (tempProbe + tempPlate) / 2 + 273.15;
if ~exist('f6')
    f6 = figure('Color', [1 1 1]);
else
    figure(f6);
    hold on
end
set(gca, 'fontsize', 15);
plot(Tavg(indeces), Zcalc(indeces) .* Tavg(indeces), '-x', 'markersize', 10, 'linewidth', 2.0, 'Color', colour(i,:));
hold on;
xlabel('Average Temperature (K)');
ylabel('Figure of Merit ZT');
finalZTy(1:length(indeces),i) = Zcalc(indeces);
finalZTx(1:length(indeces),i) = Tavg(indeces);
ZTavg = mean(Zcalc(indeces) .* Tavg(indeces))
D.10. Thermoelectric Calibration and Analysis

```matlab
if doConductivity == true
    % Electrical conductivity vs. Average Temperature
    if ~exist('f10')
        f10 = figure('Color', [1 1 1]);
    else
        figure(f10);
        hold on
    end
    set(gca, 'fontsize', 15);
    anECondTemp = [];
    anECond = [];
    for n = 1:length(indeces)
        anECondTemp(n) = (tempProbe(indeces(n)) + tempPlate(indeces(n))) / 2;
        anECond(n) = elecConductance(indeces(n)) / area * thickness / 100;
    end
    semilogy(anECondTemp, anECond, '-x', 'markersize', 10, 'linewidth', 2.0, 'Color', colour(i,:));
    hold on;
    xlabel('Average Temperature (degC)');
    ylabel('Electrical Conductivity (S/cm)');
    finalECy(1:length(indeces),i) = anECond;
    finalECx(1:length(indeces),i) = anECondTemp + 273.15;
end
```

% Thermal conductivity vs. Average Temperature
```
if ~exist('f11')
    f11 = figure('Color', [1 1 1]);
else
    figure(f11);
hold on
```

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D.10. Thermoelectric Calibration and Analysis

```matlab
end

set(gca, 'fontsize', 15);
anTCondTemp = []; anTCond = [];
for n = 1:(length(indeces)-1)
    anTCondTemp(n) = (tempProbe(indeces(n)) + tempProbe(indeces(n+1)) + tempPlate(indeces(n)) + tempPlate(indeces(n+1))) / 4;
anTCond(n) = (heaterPower(indeces(n+1)) - heaterPower(indeces(n))) / (tempDelta(indeces(n+1)) - tempDelta(indeces(n))) / area * thickness;
end

plot(anTCondTemp, anTCond, '-x', 'markersize', 10, 'linewidth', 2.0, 'Color', colour(i,:));
hold on;
xlabel('Average Temperature (degC)');
ylabel('Thermal Conductivity (W/mK)');
finalTCy(1:length(indeces)-1,i) = anTCond;
finalTCx(1:length(indeces)-1,i) = anTCondTemp + 273.15;

% Seebeck coefficient vs. Average Temperature
if ~exist('f12')
    f12 = figure('Color', [1 1 1]);
else
    figure(f12);
    hold on
end
set(gca, 'fontsize', 15);
anSeebeckTemp = []; anSeebeck = [];
for n = 1:(length(indeces)-1)
    anSeebeckTemp(n) = (tempProbe(indeces(n)) + tempProbe(indeces(n))) / 2;
anSeebeck(n) = (heaterPower(indeces(n+1)) - heaterPower(indeces(n))) / (tempDelta(indeces(n+1)) - tempDelta(indeces(n))) / area * thickness;
end
plot(anSeebeckTemp, anSeebeck, '-x', 'markersize', 10, 'linewidth', 2.0, 'Color', colour(i,:));
hold on;
xlabel('Average Temperature (degC)');
ylabel('Seebeck Coefficient (V/K)');
finalTCy(1:length(indeces)-1,i) = anSeebeck;
finalTCx(1:length(indeces)-1,i) = anSeebeckTemp + 273.15;
```
D.10. Thermoelectric Calibration and Analysis

\[ \text{anSeebeck}(n) = \left( \frac{\text{elecVoltage}(\text{indeces}(n+1)) - \text{elecVoltage}(\text{indeces}(n))}{\text{tempDelta}(\text{indeces}(n+1)) - \text{tempDelta}(\text{indeces}(n))} \right) * 1e6 + 3.5; \]

\end{verbatim}

\begin{verbatim}
322\text{plot}(\text{anSeebeckTemp}, \text{anSeebeck}, '-x', 'markersize', 10, 'linewidth', 2.0, 'Color', \text{colour}(i,:));
323\text{hold} on;
324\text{xlabel}('Average Temperature (degC)');
325\text{ylabel}('Seebeck Coefficient (\mu V/K)');
326\text{finalSeebecky}(1: \text{length(indeces)}-1,i) = \text{anSeebeck};
327\text{finalSeebeckx}(1: \text{length(indeces)}-1,i) = \text{anSeebeckTemp} + 273.15;
\end{verbatim}

\begin{verbatim}
331\text{end end end end}
332\text{end}
333\text{$\%$Legends}
334\begin{verbatim}
335\text{figure}(f1);
336\text{set}(\text{gca}, 'fontsize', 10);
337\text{legs} = [];
338\text{for} j = 1:len
339\text{legs}{end+1} = \text{sprintf}('\%s: Probe', \text{names}{j});
340\text{legs}{end+1} = \text{sprintf}('\%s: Plate', \text{names}{j});
341\text{if} ~\text{isempty}(\text{indeces})
342\text{legs}{end+1} = \text{sprintf}('\%s: Sample', \text{names}{j});
343\text{end}
344\text{end}
345\text{legend}(\text{legs}, 'location', 'northwest');
346\text{figure}(f2)
347\text{set}(\text{gca}, 'fontsize', 10);
348\text{legs} = [];
\end{verbatim}

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for j = 1:len
    legs{end+1} = sprintf('%s', names{j});
  if ~isempty(indeces)
    legs{end+1} = sprintf('%s: Sample', names{j});
  end
end
legend(legs, 'location', 'northwest');

if ~isempty(indeces)
  figure(f3)
  set(gca, 'fontsize', 10);
  legs = [];
  for j = 1:len
    %legs{end+1} = sprintf('%s: Experimental', names{j});
    legs{end+1} = sprintf('%s', names{j});
    %legs{end+1} = sprintf('%s: Linear Fit', names{j});
  end
  legend(legs, 'location', 'northwest');
end

figure(f4)
set(gca, 'fontsize', 10);
legs = [];
for j = 1:len
  legs{end+1} = sprintf('%s', names{j});
end
legend(legs, 'location', 'northwest');

figure(f5)
set(gca, 'fontsize', 10);
legs = [];
for j = 1:len
  %legs{end+1} = sprintf('%s: Experimental', names{j});
  legs{end+1} = sprintf('%s', names{j});
  %legs{end+1} = sprintf('%s: Linear Fit', names{j});
end
```
legend(legs, 'location', 'northwest');

figure(f6)
set(gca, 'fontsize', 10);
legs = [];
for j = 1:len
    legs(end+1) = sprintf('%s', names{j});
end
legend(legs, 'location', 'northwest');

figure(f10)
set(gca, 'fontsize', 10);
legs = [];
for j = 1:len
    legs(end+1) = sprintf('%s', names{j});
end
legend(legs, 'location', 'northwest');

figure(f11)
set(gca, 'fontsize', 10);
legs = [];
for j = 1:len
    legs(end+1) = sprintf('%s', names{j});
end
legend(legs, 'location', 'northwest');

figure(f12)
set(gca, 'fontsize', 10);
legs = [];
for j = 1:len
    legs(end+1) = sprintf('%s', names{j});
end
legend(legs, 'location', 'northwest');
end
```
Appendix E

Potentiostat Source Files

E.1 Front Panel
Figure E.1: Labview Front Panel of Potentiostat Application.
E.2. Labview Programming

E.2 Labview Programming
Appendix F

LAMMPS Scripts

F.1 Silicon Bulk

#Exploration of different temp fixes
#initialization
boundary p p p
units metal
echo both
newton on
log log.si_temp

#definitions
lattice diamond 5.43
atom_style atomic
read_data straight5x5x400.lammps
pair_style sw
pair_coeff * * Si.sw Si
mass 1 28.0

#Timestep and neighbours
timestep 0.001
neighbor 2.0 bin
neigh_modify every 1 delay 0 check no

#Thermo configuration
thermo 200
thermo_style custom step temp epair etotal press
thermo_modify lost ignore flush yes

#Define regions for post-processing
region pp prism -10.0 60.0 -10.0 60.0 75 125 0.0 0.0
F.1. Silicon Bulk

0.0

group ppg region pp

#npt
velocity all create 300 429349 dist gaussian
fix 1 all npt temp 300 300 0.1 z 0.0 0.0 0.1

#Equilibrate at setpoint
run 50000

#Settle
unfix 1
fix 2 all nve
fix 3 all temp/berendsen 300.0 300.0 20.0
run 25000

dump 1 ppg custom 20 dumpforce20pre.Si id mass
   x y z vx vy vz fx fy fz
dump_modify 1 sort id
run 100000
undump 1

#muller-plathe thermal conductivity

#Temp gradient
compute ke all ke/atom
variable temp atom c_ke/(1.5*8.617*10^-5)
fix 5 all ave/spatial 10 100 1000 z lower .05 v_temp
   file tmp.initprofile units reduced

#Flux
fix 4 all thermal/conductivity 200 z 20
thermo_style custom step temp etotal dt elapsed f_4
log log.warm_up

#Setup a restart file
restart 100000 tmp*.restart
run 1000000
F.2 silicon nanowire

log log.si_flux
unfix 5
fix 6 all ave/spatial 10 100 1000 z lower .02 v_temp file tmp.profile units reduced
run 200000

dump 1 ppg custom 20 dumpforce20.Si id mass
  x y z vx vy vz fx fy fz
dump_modify 1 sort id
run 25000
undump 1

F.2 silicon nanowire

#Exploration of different temp fixes

#initialization
boundary s s p
units metal
echo both
newton on
log log.si_temp

#definitions
lattice diamond 5.43
atom_style atomic
read_data straight9x9x400.lammps
pair_style sw
pair_coeff * * Si.sw Si
mass 1 28.0

#Timestep and neighbours
timestep 0.001
neighbor 2.0 bin
neigh_modify every 1 delay 0 check no

#Thermo configuration
thermo 500
thermo_style custom step temp epair etotal press
thermo_modify lost ignore flush yes
# Define regions for post-processing
region pp prism -10.0 60.0 -10.0 60.0 75 125 0.0 0.0
  0.0

# npt
velocity all create 300 429349 dist gaussian
fix 1 all npt temp 300 300 0.1 z 0.0 0.0 0.1

# Equilibrate at setpoint
run 50000

# Settle
unfix 1
fix 2 all nve
fix 3 all temp/berendsen 300.0 300.0 20.0
run 25000

# Muller-Plathe thermal conductivity

# Temp gradient
compute ke all ke/atom
variable temp atom c_ke/(1.5*8.617*10^-5)
fix 5 all ave/spatial 10 100 1000 z lower .05 v_temp

file tmp.initprofile units reduced

# Flux
fix 4 all thermal/conductivity 500 z 20
thermo_style custom step temp etotal dt elapsed f_4
log log.warm_up

# Setup a restart file
restart 100000 tmp*.restart
run 1000000

log log.si_flux
unfix 5
fix 6 all ave/spatial 10 100 1000 z lower .02 v_temp
F.3. ZnO Bulk

```plaintext
# REAX potential for ZnO system - Mueller Plathe conductivity
# ......

units          real
boundary       p p p
echo           both
newton         on

atom_style    charge
read_data      ZnObulk8x8x300.lammps

pair_style    reax/c NULL
pair_coeff     * * ffield.reax 0 Zn

#1 fs steps
timestep       0.5
neighbor       2.0 bin
neigh_modify   every 20 delay 0 check no

thermo         2000
thermo_style   custom step temp epair etotal press
thermo_modify  lost ignore flush yes

velocity       all create 300 43249349 dist gaussian
fix            1 all npt temp 300.0 300.0 500.0 tri 0.0 0.0 1000.0
fix            2 all qeq/reax 1 0.0 10.0 1e-6 reax/c

# Equilibrate temperature at setpoint
run            400000
```

F.3. ZnO Bulk
unfix 1

#Settle
fix 3 all npt temp 300.0 300.0 20000.0
   tri 0.0 0.0 5000.0 drag 2.0
#fix 7 all temp/berendsen 300.0 300.0 20000.0
#fix 8 all press/berendsen 0.0 0.0 1000.0
run 50000

#LDOS_EMD
dump 1 all custom 40 dumpforce40pre.ZnO id type mass
   x y z vx vy vz fx fy fz
dump_modify 1 sort id
run 50000
undump 1

#Temperature gradient
compute ke all ke/atom
variable temp atom c_ke*0.043/1.5/8.617e-5
fix 4 all ave/spatial 10 100 1000 z lower .05 v_temp
   file tmp.initprofile units reduced

#Flux
fix 5 all thermal/conductivity 2000 z 20
thermo_style custom step temp etotal dt elapsed f_5
#thermo_modify lost ignore flush yes
log log.warm_up

#Setup restart file before long haul
restart 200000 tmp*.restart
run 2000000

log log.si_flux
unfix 4
fix 6 all ave/spatial 10 100 1000 z lower .02 v_temp
   file tmp.profile units reduced
run 600000

dump 1 all custom 40 dumpforce40.ZnO id type mass
x y z vx vy vz fx fy fz
run 50000
undump 1
log log.end

# Try relaxing at the end
variable ulx equal "lx"
variable uly equal "ly"
variable ulz equal "lz"
variable ulxy equal "xy"
print "Box lengths (x/y/z/xy): ${ulx}/${uly}/${ulz}/${ulxy}"

fix 10 all box/relax tri 0.0 nreset 100
minimize 1e-30 1e-30 5000 10000
unfix 10

print "Box lengths (x/y/z/xy): ${ulx}/${uly}/${ulz}/${ulxy}"
thermo 4000
thermo_style custom step temp epair etotal press
thermo_modify lost ignore flush yes

#Setup region for export
lattice diamond 5.30
region pp prism -50.0 50.0 -50.0 50.0 25 175 0.0 0.0 0.0

group ppg region pp

velocity all create 300 43249349 dist gaussian
fix 1 all npt temp 300.0 300.0 500.0 z 0.0 0.0 500.0
fix 2 all qeq/reax 1 0.0 10.0 1e-6 reax/c

#Equilibriate temperature at setpoint
run 100000
unfix 1

#Settle
fix 3 all nve
fix 7 all temp/berendsen 300.0 300.0 20000.0
run 50000

#LDOS_EMD
dump 1 all custom 40 dumpforce40pre.ZnO id type mass
    x y z vx vy vz fx fy fz
dump_modify 1 sort id
derun 50000
undump 1

#Temperature gradient
compute ke all ke/atom
variable temp atom c_ke*0.043/1.5/8.617e-5
fix 4 all ave/spatial 10 100 1000 z lower .05 v_temp
    file tmp.initprofile units reduced

#Flux
fix 5 all thermal/conductivity 4000 z 20
thermo_style custom step temp etotal dt elapsed f_5
#thermo_modify lost ignore flush yes
F.5. ZnO LDOS-EMD Void Simulation

```
log              log.warm_up

#Setup restart file before long haul
restart 2000000 tmp*.restart
run 2000000

log              log.si_flux
unfix             4
fix 6 all ave/spatial 10 100 1000 z lower .02 v_temp
file tmp.profile units reduced
run 600000

dump 1 all custom 40 dumpforce40.ZnO id type mass
x y z vx vy vz fx fy fz
dump_modify 1 sort id
run 500000
undump 1
```

F.5 ZnO LDOS-EMD Void Simulation

```
units     real
boundary  s s p
echo      both
newton    on

atom_style  charge
read_data   ZnOstraightHex5x5x200.lammps

pair_style reax/c NULL
pair_coeff  * * ffield.reax 0 Zn

timestep 0.5
neighbor  2.0 bin
neigh_modify every 20 delay 0 check no

velocity all create 300 2347623 dist gaussian
fix 1 all npt temp 300.0 300.0 500.0 z 0.0 0.0 0.0
fix 2 all qeq/reax 1 0.0 10.0 1e-6 reax/c
```
### F.5. ZnO LDOS-EMD Void Simulation

<table>
<thead>
<tr>
<th>Line</th>
<th>Command</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>run</td>
<td>100000</td>
</tr>
<tr>
<td>21</td>
<td>unfix 1</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>fix</td>
<td>3 all nve</td>
</tr>
<tr>
<td>23</td>
<td>fix</td>
<td>7 all temp/berendsen 300.0 300.0 20000.0</td>
</tr>
<tr>
<td>24</td>
<td>run</td>
<td>50000</td>
</tr>
<tr>
<td>25</td>
<td>dump</td>
<td>1 all custom 40 dumpforce40-0.ZnO id type mass x y z vx vy vz fx fy fz</td>
</tr>
<tr>
<td>26</td>
<td>dump_modify</td>
<td>1 sort id</td>
</tr>
<tr>
<td>27</td>
<td>run</td>
<td>50000</td>
</tr>
<tr>
<td>28</td>
<td>undump</td>
<td>1</td>
</tr>
<tr>
<td>29</td>
<td>region reg1</td>
<td>sphere 9.58967 13.75236 920.75782 8.12342</td>
</tr>
<tr>
<td></td>
<td>side in</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>delete_atoms reg1</td>
<td>compress no</td>
</tr>
<tr>
<td>31</td>
<td>region reg2</td>
<td>sphere -6.86354 -10.82704 456.00554 7.60941</td>
</tr>
<tr>
<td></td>
<td>side in</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>delete_atoms reg2</td>
<td>compress no</td>
</tr>
<tr>
<td>33</td>
<td>region reg3</td>
<td>sphere 0.58229 1.16534 588.30192 8.17354</td>
</tr>
<tr>
<td></td>
<td>side in</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>delete_atoms reg3</td>
<td>compress no</td>
</tr>
<tr>
<td>35</td>
<td>region reg4</td>
<td>sphere 6.69980 7.17401 656.44353 7.70437</td>
</tr>
<tr>
<td></td>
<td>side in</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>delete_atoms reg4</td>
<td>compress no</td>
</tr>
<tr>
<td>37</td>
<td>region reg5</td>
<td>sphere -5.41655 13.88884 353.57454 6.87520</td>
</tr>
<tr>
<td></td>
<td>side in</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>delete_atoms reg5</td>
<td>compress no</td>
</tr>
<tr>
<td>39</td>
<td>region reg6</td>
<td>sphere -11.15004 14.12035 135.44050 7.28852</td>
</tr>
<tr>
<td></td>
<td>side in</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>delete_atoms reg6</td>
<td>compress no</td>
</tr>
<tr>
<td>41</td>
<td>region reg7</td>
<td>sphere -11.01819 -5.34767 416.98654 9.58458</td>
</tr>
<tr>
<td></td>
<td>side in</td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>delete_atoms reg7</td>
<td>compress no</td>
</tr>
<tr>
<td>43</td>
<td>region reg8</td>
<td>sphere -3.96855 14.16860 30.43652 7.40674</td>
</tr>
<tr>
<td></td>
<td>side in</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>delete_atoms reg8</td>
<td>compress no</td>
</tr>
<tr>
<td>45</td>
<td>region reg9</td>
<td>sphere -3.05698 8.50387 994.49663 7.27876</td>
</tr>
<tr>
<td></td>
<td>side in</td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>delete_atoms reg9</td>
<td>compress no</td>
</tr>
</tbody>
</table>
region reg10 sphere -1.73402 -4.18242 848.57697 8.55296
side in
del‌‌eat‌‌_atoms region reg10 compress no
run 100000
dump 1 all custom 40 dumpforce40-11.ZnO id type mass
   x y z vx vy vz fx fy fz
dump_modify 1 sort id
run 50000
undump 1
region reg11 sphere -11.07604 4.38182 842.77047 6.12803
side in
del‌‌eat‌‌_atoms region reg11 compress no
region reg12 sphere -1.14410 9.17186 1047.24309 8.33586
side in
del‌‌eat‌‌_atoms region reg12 compress no
region reg13 sphere -11.84073 0.34437 199.33548 8.50822
side in
del‌‌eat‌‌_atoms region reg13 compress no
region reg14 sphere -7.31064 -7.24285 567.95003 6.40155
side in
del‌‌eat‌‌_atoms region reg14 compress no
region reg15 sphere 5.93615 13.01047 999.27870 7.49895
side in
del‌‌eat‌‌_atoms region reg15 compress no
region reg16 sphere 2.45887 5.87995 540.86965 7.88357
side in
del‌‌eat‌‌_atoms region reg16 compress no
region reg17 sphere -12.61216 -9.37619 460.61086
   7.72597 side in
del‌‌eat‌‌_atoms region reg17 compress no
region reg18 sphere -8.06651 2.48307 634.62588 8.88370
side in
del‌‌eat‌‌_atoms region reg18 compress no
region reg19 sphere -4.97175 -0.73489 871.59239 8.34852
side in
del‌‌eat‌‌_atoms region reg19 compress no
region reg20 sphere 5.30332 1.99199 879.30346 8.88271
side in
delete_atoms region reg20 compress no
run 100000
dump 1 all custom 40 dumpforce40-21.ZnO id type mass x y z vx vy vz fx fy fz
dump_modify 1 sort id
run 50000
undump 1
region reg21 sphere 9.40560 -5.89620 316.24485 7.90322 side in
delete_atoms region reg21 compress no
region reg22 sphere -0.16424 4.48536 867.51734 8.11090 side in
delete_atoms region reg22 compress no
region reg23 sphere 11.27876 7.45672 189.36143 8.47890 side in
delete_atoms region reg23 compress no
region reg24 sphere 1.59944 8.48446 854.49906 7.19450 side in
delete_atoms region reg24 compress no
region reg25 sphere -9.28628 5.19725 8.80125 9.15433 side in
delete_atoms region reg25 compress no
region reg26 sphere 0.05335 14.48624 1042.41695 6.90831 side in
delete_atoms region reg26 compress no
region reg27 sphere 8.98690 9.75339 250.14258 8.62741 side in
delete_atoms region reg27 compress no
region reg28 sphere 12.25375 7.66691 101.30133 8.00242 side in
delete_atoms region reg28 compress no
region reg29 sphere -0.96659 -11.10066 1047.60582 9.51048 side in
delete_atoms region reg29 compress no
region reg30 sphere -7.26202 4.42633 499.95082 7.43644 side in
F.5. ZnO LDOS-EMD Void Simulation

```plaintext
delete_atoms region reg30 compress no
run 100000
dump 1 all custom 40 dumpforce40-31.Zn0 id type mass x y z vx vy vz fx fy fz
dump_modify 1 sort id
run 50000
undump 1

region reg31 sphere 0.75223 3.38489 882.99768 6.25125 side in
delete_atoms region reg31 compress no
region reg32 sphere 2.73149 1.81301 169.80810 6.58178 side in
delete_atoms region reg32 compress no
region reg33 sphere 3.53975 11.55326 34.81551 7.71209 side in
delete_atoms region reg33 compress no
region reg34 sphere 9.70429 1.11694 389.37595 6.96260 side in
delete_atoms region reg34 compress no
region reg35 sphere -11.60141 -6.62148 589.80505 8.12034 side in
delete_atoms region reg35 compress no
region reg36 sphere 1.13561 -3.44009 916.76363 9.38779 side in
delete_atoms region reg36 compress no
region reg37 sphere -0.88081 8.17511 830.05448 7.47239 side in
delete_atoms region reg37 compress no
region reg38 sphere -8.28660 -4.62605 251.15603 7.56758 side in
delete_atoms region reg38 compress no
region reg39 sphere -12.65494 -3.90649 568.93076 7.69224 side in
delete_atoms region reg39 compress no
region reg40 sphere 0.81730 7.88542 986.45799 7.30399 side in
delete_atoms region reg40 compress no
```

F.5. ZnO LDOS-EMD Void Simulation

run 100000
dump 1 all custom 40 dumpforce40-41.ZnO id type mass
   x y z vx vy vz fx fy fz
dump_modify 1 sort id
run 50000
undump 1
region reg41 sphere -5.89167 1.10966 645.78051 6.74900
   side in
delete_atoms region reg41 compress no
region reg42 sphere -12.12108 -5.88121 259.64491 7.74532 side in
   delete_atoms region reg42 compress no
region reg43 sphere 3.36226 -3.37921 1033.37675 9.48459
   side in
delete_atoms region reg43 compress no
region reg44 sphere 3.10040 -2.44283 179.80060 8.63892
   side in
delete_atoms region reg44 compress no
region reg45 sphere 5.53273 -9.42230 821.09847 9.55452
   side in
delete_atoms region reg45 compress no
region reg46 sphere 3.39551 6.94233 914.66637 9.79490
   side in
delete_atoms region reg46 compress no
region reg47 sphere -3.80381 -9.59946 329.40190 6.68340
   side in
delete_atoms region reg47 compress no
region reg48 sphere -3.23443 1.82221 837.38630 9.80993
   side in
delete_atoms region reg48 compress no
region reg49 sphere -5.39740 13.32796 194.96233 7.76025
   side in
delete_atoms region reg49 compress no
region reg50 sphere -8.15341 -4.42625 18.22766 6.98512
   side in
delete_atoms region reg50 compress no
F.5. ZnO LDOS-EMD Void Simulation

run 100000

dump 1 all custom 40 dumpforce40-51.ZnO id type mass x y z vx vy vz fx fy fz
dump_modify 1 sort id
run 50000
undump 1

region reg51 sphere -2.91437 1.64751 321.54849 6.05216
side in
delete_atoms region reg51 compress no
region reg52 sphere 9.67751 -5.05684 231.88738 6.01666
side in
delete_atoms region reg52 compress no
region reg53 sphere -6.16241 -4.05796 607.43857 8.08163
side in
delete_atoms region reg53 compress no
region reg54 sphere 7.68422 8.86812 985.25385 8.10284
side in
delete_atoms region reg54 compress no
region reg55 sphere 11.16970 9.84449 200.37073 8.78998
side in
delete_atoms region reg55 compress no
region reg56 sphere 10.65647 12.07059 912.81977 8.59055
side in
delete_atoms region reg56 compress no
region reg57 sphere 11.81389 -4.69934 738.74435 6.49453
side in
delete_atoms region reg57 compress no
region reg58 sphere 4.17987 7.10381 711.84855 7.99260
side in
delete_atoms region reg58 compress no
region reg59 sphere -2.27522 11.13656 497.61562 7.27129
side in
delete_atoms region reg59 compress no
region reg60 sphere -11.62952 5.80652 800.39043 8.01549
side in
delete_atoms region reg60 compress no

run 100000
dump 1 all custom 40 dumpforce40-61.ZnO id type mass
   x y z vx vy vz fx fy fz
dump_modify 1 sort id
run 50000
undump 1

region reg61 sphere 5.89271 5.30744 531.97481 6.75317
   side in
delete_atoms region reg61 compress no
region reg62 sphere -3.66680 7.61950 795.09003 6.21251
   side in
delete_atoms region reg62 compress no
region reg63 sphere -1.84547 4.52116 775.72199 7.59667
   side in
delete_atoms region reg63 compress no
region reg64 sphere 1.14081 -1.39874 360.25635 7.30489
   side in
delete_atoms region reg64 compress no
region reg65 sphere 8.23368 -9.13301 38.52330 8.74027
   side in
delete_atoms region reg65 compress no
region reg66 sphere -3.51832 13.02894 180.63364 7.64666
   side in
delete_atoms region reg66 compress no
region reg67 sphere -2.60476 1.99176 166.21762 9.93066
   side in
delete_atoms region reg67 compress no
region reg68 sphere 3.40909 12.75413 677.65477 8.54359
   side in
delete_atoms region reg68 compress no
region reg69 sphere 2.59366 -4.79695 303.68689 6.66733
   side in
delete_atoms region reg69 compress no
region reg70 sphere 5.32911 10.86586 232.46415 6.24833
   side in
delete_atoms region reg70 compress no
run 100000

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F.5. ZnO LDOS-EMD Void Simulation

```plaintext
dump 1 all custom 40 dumpforce40-71.ZnO id type mass
   x y z vx vy vz fx fy fz
dump_modify 1 sort id
run 50000
undump 1

region reg71 sphere -2.47919 13.67968 153.20752 8.22190
   side in
delete_atoms region reg71 compress no
region reg72 sphere 7.10294 -6.11449 369.42886 6.89069
   side in
delete_atoms region reg72 compress no
region reg73 sphere -0.84928 12.89458 668.66503 6.44214
   side in
delete_atoms region reg73 compress no
region reg74 sphere -4.03760 6.95261 1053.52689 7.44801
   side in
delete_atoms region reg74 compress no
region reg75 sphere 0.48677 -5.37180 368.08301 6.53168
   side in
delete_atoms region reg75 compress no
region reg76 sphere -8.10378 -3.44372 51.46356 7.11120
   side in
delete_atoms region reg76 compress no
region reg77 sphere -10.70575 -10.37128 1021.84694
   7.30559 side in
delete_atoms region reg77 compress no
region reg78 sphere 4.84083 -3.93668 466.39804 9.27713
   side in
delete_atoms region reg78 compress no
region reg79 sphere 7.53624 2.38863 374.82191 7.30082
   side in
delete_atoms region reg79 compress no
region reg80 sphere 9.83733 -8.24476 405.52211 6.16304
   side in
delete_atoms region reg80 compress no
run 100000
dump 1 all custom 40 dumpforce40-81.ZnO id type mass
```

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F.5. ZnO LDOS-EMD Void Simulation

```plaintext
x y z vx vy vz fx fy fz
dump_modify 1 sort id
run 50000
undump 1

region reg81 sphere 3.44562 13.07543 602.64936 7.45290
   side in
delete_atoms region reg81 compress no
region reg82 sphere -4.80464 6.93522 156.26686 8.88441
   side in
delete_atoms region reg82 compress no
region reg83 sphere -8.65539 -3.94574 1029.85175 7.32466 side in
delete_atoms region reg83 compress no
region reg84 sphere 11.84194 11.97176 200.10571 6.14063
   side in
delete_atoms region reg84 compress no
region reg85 sphere -3.23414 6.66891 1006.87828 7.43141
   side in
delete_atoms region reg85 compress no
region reg86 sphere -3.37378 -7.55900 801.39120 7.87329
   side in
delete_atoms region reg86 compress no
region reg87 sphere -0.47312 -6.29566 57.65066 8.74613
   side in
delete_atoms region reg87 compress no
region reg88 sphere -0.43598 10.12661 29.42383 9.33051
   side in
delete_atoms region reg88 compress no
region reg89 sphere 8.71628 -3.99842 350.02381 8.90360
   side in
delete_atoms region reg89 compress no
region reg90 sphere 6.11486 9.28708 88.96446 7.82487
   side in
delete_atoms region reg90 compress no
run 100000
dump 1 all custom 40 dumpforce40-91.ZnO id type mass
   x y z vx vy vz fx fy fz
```
dump_modify 1 sort id
run 50000
undump 1

region
  side in
delete_atoms
  region reg91 compress no
region
  side in
delete_atoms
  region reg92 compress no
region
  reg93 sphere 4.37113 -10.95040 446.79831 8.78571
  side in
delete_atoms
  region reg93 compress no
region
  reg94 sphere -12.72318 -2.79687 151.10708 6.47825 side in
delete_atoms
  region reg94 compress no
region
  reg95 sphere 11.28137 -9.20721 502.78053 7.34620
  side in
delete_atoms
  region reg95 compress no
region
  reg96 sphere 11.11559 3.84237 720.03555 7.84932
  side in
delete_atoms
  region reg96 compress no
region
  reg97 sphere 4.25876 -9.46927 556.07950 9.47560
  side in
delete_atoms
  region reg97 compress no
region
  reg98 sphere 0.74225 -0.81037 95.30310 8.61111
  side in
delete_atoms
  region reg98 compress no
region
  reg99 sphere 4.73087 6.81487 261.16374 7.63110
  side in
delete_atoms
  region reg99 compress no
region
  reg100 sphere -0.58602 -3.86730 415.04570 6.22966 side in
delete_atoms
  region reg100 compress no
run 100000
dump 1 all custom 40 dumpforce40-101.ZnO id type mass
  x y z vx vy vz fx fy fz
dump_modify 1 sort id
F.5. ZnO LDOS-EMD Void Simulation

run 50000
undump 1

region reg101 sphere -0.01593 -0.39385 426.32939 6.77240 side in
delete_atoms region reg101 compress no
region reg102 sphere -0.05633 5.52126 670.67089 9.41748 side in
delete_atoms region reg102 compress no
region reg103 sphere -12.35492 -5.95420 620.10457 9.71651 side in
delete_atoms region reg103 compress no
region reg104 sphere 9.42646 0.45215 1048.85303 6.57157 side in
delete_atoms region reg104 compress no
region reg105 sphere -4.80459 -11.09594 391.26692 6.93131 side in
delete_atoms region reg105 compress no
region reg106 sphere -6.16781 13.63507 366.83408 6.01930 side in
delete_atoms region reg106 compress no
region reg107 sphere 3.84623 13.05462 536.02203 8.70065 side in
delete_atoms region reg107 compress no
region reg108 sphere 12.29758 -0.12546 812.45211 6.28170 side in
delete_atoms region reg108 compress no
region reg109 sphere 2.96361 -1.22613 949.13525 7.23869 side in
delete_atoms region reg109 compress no
region reg110 sphere -5.88513 -1.79684 32.91701 7.39146 side in
delete_atoms region reg110 compress no
run 100000
dump 1 all custom 40 dumpforce40-111.ZnO id type mass x y z vx vy vz fx fy fz
dump_modify 1 sort id
run 50000
F.5. ZnO LDOS-EMD Void Simulation

undump 1
region reg111 sphere -7.69200 9.82949 107.11621 6.12598
side in
delete_atoms region reg111 compress no
region reg112 sphere 0.16084 4.44133 510.12644 6.56107
side in
delete_atoms region reg112 compress no
region reg113 sphere 0.85426 9.56083 901.54587 9.56247
side in
delete_atoms region reg113 compress no
region reg114 sphere 7.38728 13.12272 345.40963 6.70209
side in
delete_atoms region reg114 compress no
region reg115 sphere 5.71600 4.67430 19.41394 9.52331
side in
delete_atoms region reg115 compress no
region reg116 sphere 5.89015 -1.42195 682.62602 7.78644
side in
delete_atoms region reg116 compress no
region reg117 sphere -8.35761 0.06757 437.02722 6.07279
side in
delete_atoms region reg117 compress no
region reg118 sphere -12.80974 8.16867 815.68458 8.75926
side in
delete_atoms region reg118 compress no
region reg119 sphere -8.05302 6.32038 33.72089 9.52750
side in
delete_atoms region reg119 compress no
region reg120 sphere -12.15768 4.08469 38.16021 8.47247
side in
delete_atoms region reg120 compress no
run 100000
dump 1 all custom 40dumpforce40-121.ZnO id type mass x y z vx vy vz fx fy fz
dump_modify 1 sort id
run 50000
undump 1
F.5. ZnO LDOS-EMD Void Simulation

region reg121 sphere -12.25510 6.05248 612.11770
  7.90616 side in
delete_atoms region reg121 compress no
region reg122 sphere -5.23620 0.67595 870.54856 7.48712
  side in
delete_atoms region reg122 compress no
region reg123 sphere -8.88042 6.42184 638.03515 8.18671
  8.61608 side in
delete_atoms region reg123 compress no
region reg124 sphere -0.04175 -5.92361 805.82573
  8.61608 side in
delete_atoms region reg124 compress no
region reg125 sphere 9.56809 4.75248 707.91645 7.49780
  7.49780 side in
delete_atoms region reg125 compress no
region reg126 sphere -3.64223 0.13359 565.80587 9.98841
  9.11057 side in
delete_atoms region reg126 compress no
region reg127 sphere -4.51550 -6.48746 144.27615
  9.11057 side in
delete_atoms region reg127 compress no
run 100000
dump 1 all custom 40 dumpforce40-131.ZnO id type mass
  x y z vx vy vz fx fy fz
dump_modify 1 sort id
run 50000
undump 1