# Laser-Induced Thermoelectric Energy Generation Using Carbon Nanotube Forests

by

Harrison Daniel Earl Fan B.A.Sc., The University of Waterloo, 2012

## A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES (Electrical and Computer Engineering)

> THE UNIVERSITY OF BRITISH COLUMBIA (Vancouver)

> > April 2015

© Harrison Daniel Earl Fan, 2015

## Abstract

Although there has been extensive research on the thermoelectric effect, there have only been some reports on the photo-thermoelectric effect in carbon nanotubes, i.e. the conversion of light to heat to electricity. A device capable of producing a thermoelectric voltage by light irradiation on a forest of aligned multi-walled carbon nanotubes has not yet been reported. The work presented in this thesis first outlines the growth conditions by which millimetre-long CNTs were grown by catalytic chemical vapour deposition (CVD). Two novel thermoelectric devices were fabricated based on two intrinsic properties of CNT forests. (1) Using the "Heat Trap" effect (light-induced heat localization), the first device induced a potential difference (few hundred  $\mu V$ ) from low incident laser power. The temporal dynamics of the induced voltage were understood to be due to a competition of the temperature gradients within the device materials. A finite element analysis model was simulated the thermal and electrical characteristics. The temperaturedependent thermal conductivity of CNTs was derived based on the experimental induced voltage and was seen to fall-off with temperature, confirming a previously-suggested mechanism for the effect. (2) Since the thermal conductivity of CNTs can be 1-2 orders of magnitude smaller in the direction perpendicular to the nanotube axis, a second device was fabricated to achieve a higher temperature gradient. Under a few hundred mW of laser power, a few mV of potential difference was induced, indicating power conversion efficiencies in the 10<sup>-5</sup> % range. A finite element analysis model was created, which by using the experimentally-derived thermal conductivity from the previous device, predicted the induced voltage to within 10% at high laser powers. Calculation of the room temperature figure-of-merit ZT was low ( $10^{-6}$ range), however no device optimization had been performed in these proof-of-concept prototypes. If CNTbased thermoelectric devices are to be used at higher temperatures, the three temperature-dependent material parameters enhance ZT and the efficiency. CNTs can be a promising material choice if cost and low toxicity are concerns, since the CVD process is fairly inexpensive and carbon-containing precursors are abundant. Moreover, CNTs have a high power-to-weight ratio and CNT forests are sparse.

# Preface

The contributions from this thesis have led to the following publications and presentations:

- 1. Amir H. Khoshaman, Harrison D. E. Fan, Andrew T. Koch, George A. Sawatzky, Alireza Nojeh. Thermionics, Thermoelectrics, and Nanotechnology - New Possibilities for Old Ideas. IEEE Nanotechnology Magazine, vol. 8, pp. 4-15, 2014.
- 2. Harrison D. E. Fan, Amir H. Khoshaman, Andrew T. Koch, Alireza Nojeh. Thermoelectric Performance of Vertically-aligned Carbon Nanotube Forests. *Conference poster* in the 97<sup>th</sup> "Canadian Chemistry Conference and Exhibition," Vancouver, British Columbia, June 2014.
- 3. Harrison D. E. Fan, Amir H. Khoshaman, Andrew T. Koch, Alireza Nojeh. Thermoelectric devices based on sandwiched carbon nanotube forests and the effect of contact electrodes. *Conference poster* in "NT14: The Fifteenth International Conference on the Science and Application of Nanotubes," Los Angeles, California, June 2014.

All of the chapters were written by the author with the assistance of Professor Alireza Nojeh. All of the experiments were conceived by the author with assistance from Mr. Amir Khoshaman and Mr. Andrew Koch, and guidance from Professor Alireza Nojeh. Parts of Chapter 3 of the thesis contain some results from the above conference posters. The author analyzed the data and discussed them with Mr. Amir Khoshaman, Mr. Andrew Koch, and Professor Alireza Nojeh.

# Table of Contents

Abstract		ii
Preface.		ii
Table of	Contents	iv
List of T	ables	vi
List of F	gures	vii
List of S	ymbols and Constants	xi
List of A	bbreviations	xiii
Acknow	edgements	xiv
Dedicati	)n	XV
Chapter	1 – Introduction	1
1.1.	Motivation	1
1.2.	The Thermoelectric Effect	2
1.3.	Quantifying the Performance of the Thermoelectric Effect	4
1.4.	Nanostructured Thermoelectrics	6
1.5.	Carbon Nanotube-Based Thermoelectrics	7
1.6.	The "Heat Trap" effect	
1.7.	Comparison with Thermionic Energy Conversion	9
1.8.	Objectives	
1.9.	Thesis Outline	
Chapter	2 – Carbon Nanotube Fabrication	
2.1.	Introduction	
2.2.	CNT Growth	
2.3.	Chemical Vapour Deposition Apparatus	
2.4.	Gas Flow Rate Calibration	16
2.5.	CNT Growth Recipe	
2.6.	Temperature Optimization	
2.7.	Results of CVD-Grown CNTs	23
Chapter	3 – Experimentally-Measured Thermoelectric Parameters of the Carb	on Nanotube Forest
3.1.	Introduction	
3.2.	Theory Behind the Seebeck Coefficient	
33	Experimental Measurement of the Seebeck Coefficient	26
3.3.1	Effective Seebeck Coefficient	
3.3.2	Experimental Results in Ambient	
3.3.3	Experimental Results in Vacuum	
3.4.	Experimental Measurement of Electrical Conductivity	
3.4.1	Experimental Results in Ambient	
3.5.	Theory Behind the Thermal Conductivity	
3.6.	Summary	
Chapter	4 – A "Heat Trap" Thermoelectric Energy Converter Using Carbon N	anotube Arrays 43

4.1.	Introduction	.43
4.2.	"Heat Trap" – Localized Laser Heating Under Vacuum	.43
4.3.	Longitudinal Conduction	.45
4.4.	Perpendicular Conduction	.51
4.5.	Summary	.56
Chapter	5 – Simulation Study	.57
5.1.	Introduction	.57
5.1.1	Heat Transfer Module Definitions	.57
5.1.2	AC/DC Module Definitions	.58
5.1.3	Thermoelectric Multiphysics Coupling Definitions	. 59
5.2.	Material Parameters Definitions	. 59
5.3.	Longitudinal Conduction Device Model	.61
5.3.1	Model 1: Room Temperature Reference Material Parameters	.62
5.3.2	Model 2: Room Temperature Experimental Material Parameters	.64
5.3.3	Model 3: Room Temperature Experimental Material Parameters, Tuned $\kappa_{CNT}$	.65
5.3.4	Model 4: Temperature-Dependent Material Parameters, Tuned $\kappa_{CNT}$	.66
5.4.	Perpendicular Conduction Device Model	. /1
5.4.1	Model 5: Perpendicular Conduction with ITO Electrodes	.12
5.5	Future Model Improvements	. 10 87
5.5.	Summary	. 02
5.0.	Summary	.05
Chapter	6 – Summary, Conclusion, and Future Work	.87
6.1.	Contributions	. 87
6.2.	Conclusion and Future Work	. 88
Reference	es	.90
Appendi	x A	.98
Effect of	Compression	.98
Appendi	x B	.99
COMSO	L Longitudinal Conduction Model – Data	.99
Appendi	x C	100
COMSO	L Perpendicular Conduction Model – Data	100

# List of Tables

Table 1: MWCNT growth parameters from the literature    19
Table 2: SWCNT growth parameters from the literature
Table 3: Room temperature reference material parameters to calculate effective Seebeck coefficients 29
Table 4: Experimental electrical conductivity measurements of thermoelectric materials
Table 5: Literature survey of experimental thermal conductivity of aligned MWCNTs41
Table 6: Exponential fitting parameters used to determine RC time constants       50
Table 7: Room temperature material parameters, where [] denotes from a reference, [*] denotes from COMSOL built-in, and () denotes from experiment
Table 8: Comparison of COMSOL model material properties    62
Table 9: Indium tin oxide room temperature material parameters
Table 10: Model 1 (reference room temperature material properties)
Table 11: Model 2 (experimental room temperature material properties)    99
Table 12: Model 3 (experimental room temperature material properties, tuned thermal conductivity) 99
Table 13: Model 4 (reference and experimental temperature-dependant material properties, tuned thermal conductivity)
Table 14: Model 5 (reference room temperature ITO material properties)    100

# List of Figures

Figure 1: Schematic of Seebeck effect with metal A and B
Figure 2: Schematic diagram of (left) Seebeck power generation device and (right) Peltier refrigeration device, © 2014 IEEE, with permission from Khoshaman, et al. [3]
Figure 3: Power generation efficiency vs. ZT <sub>m</sub> at varying T <sub>hot</sub>
Figure 4: CVD gas plumbing schematic
Figure 5: Photo of CVD apparatus in lab16
Figure 6: Ball flow meter flow rates reported by (red X's) manufacturer and (blue O's) measured for (a) Ar, (b) $H_2$ , (c) $C_2H_4$
Figure 7: Analog MKS MFC flow rates measured using digital MFC at varying setpoints for (a) Ar, (b) H <sub>2</sub> , (c) C <sub>2</sub> H <sub>4</sub>
Figure 8: Photos of (left) CNT forest samples growing in Zone 2, (right) high aspect ratio fully grown CNT forest
Figure 9: Screenshot of LabVIEW CVD program in "Process Run" mode
Figure 10: (a) Voltage, (b) current, (c) power, (d) average CNT height as functions of measured Zone 2 temperature
Figure 11: Photos of CNT sidewalls grown at varying Zone 2 temperatures
Figure 12: SEM micrographs of MWCNT forest sidewalls showing (top left) high anisotropic nature of CNTs, (top right) cracked sidewall edge, (bottom left) close-up of bundles of CNTs, (bottom right) damage from laser irradiation
Figure 13: Bright field TEM images
Figure 14: Measuring Seebeck coefficient in ambient using (left) digital hot plate and (right) insulated silicon wafer heating sources
Figure 15: Measuring thermoelectric voltage in the longitudinal direction under high-vacuum, (left) photo of sample holder and (right) electrical schematic, where the green ellipse represents the shape of the focused laser beam
Figure 16: Measuring thermoelectric voltage in the perpendicular direction under high-vacuum, (left) photo of sample holder and (right) electrical schematic, where the green ellipse represents the shape of the focused laser beam
Figure 17: (left) Temperature dependence of copper absolute Seebeck coefficient [82], (right) temperature dependence of copper (red X's) and silicon (blue O's) thermal conductivity [84]30
Figure 18: (left) Cu-Si-Cu potential difference vs. temperature gradient, (right) effective Seebeck coefficient vs. average temperature
Figure 19: (left) Cu-CNT-Cu potential difference vs. temperature gradient, (right) effective Seebeck coefficient vs. average temperature
Figure 20: Extracting absolute Seebeck coefficient of (top) silicon (blue O's) and (bottom) CNTs (various $\Delta$ 's and +'s) assuming varying $\kappa_{CNT}$
Figure 21: Time evolution of absolute Seebeck coefficient of CNTs measured under vacuum, where open circles indicate rough and turbo pump on/off events

Figure 22: Photo of experimental four-point probe station
Figure 23: Measured voltage as a function of input current in a four-point probe setup for (left) copper and (right) silicon
Figure 24: Measured voltage as a function of input current in a four-point probe setup for (left) silicon- CNT and (right) CNT measured longitudinally (solid black line) and perpendicularly (dashed black line)
Figure 25: Temperature dependence of electrical conductivity of (a) copper [84], (b) silicon at varying room temperature resistivities [100, 101], (c) MWCNT forest [87]
Figure 26: Top view schematic of photo-thermoelectric experimental apparatus
Figure 27: (left) Measured laser power as a function of laser setpoint power, (right) photo of mounted plano-convex cylindrical lens focusing laser through vacuum chamber viewport and onto thermoelectric device-under-test
Figure 28: Experimental schematic for longitudinal conduction with symmetric copper electrodes, where the green ellipse represents the shape of the focused laser beam
Figure 29: Sample 1 – Induced voltage as a function of time for varying incident laser powers with symmetric copper electrodes
Figure 30: Sample 2 – Induced voltage as a function of time for varying incident laser powers with symmetric copper electrodes plotted on a (left) reduced time scale and (right) full time scale
Figure 31: Sample 2 – Induced voltage as a function of time for varying incident laser powers with symmetric copper electrodes, with fitted exponential functions overlaid (black)
Figure 32: Experimental schematic for perpendicular conduction with symmetric ITO electrodes in contact with (left) silicon-CNT junction and (right) with only the compressed CNT sidewall, where the green ellipse represents the shape of the focused laser beam
Figure 33: (left) Steady-state induced voltage and (right) hysteresis of induced voltage as functions of incident laser power for (top) ITO-Si/CNT-ITO and (bottom) ITO-CNT-ITO devices
Figure 34: (a) Output voltage, (b) output current, (c) internal resistance, (d) output electrical power of an ITO-CNT-ITO thermoelectric device as functions of incident laser power
Figure 35: Power conversion efficiency as a function of incident laser power, assuming 56.7% optical transmission
Figure 36: (left) 2D Gaussian plot approximation of laser beam shape, (right) surface temperature plot under incident laser power of $Q_0 = 405 \text{ mW}$
Figure 37: Perpendicular conduction device schematic sketched in 3D61
Figure 38: Model 1 (a) induced voltage difference from simulation (red X's) and experiment (blue O's), (b) (top) hot junction (red X's), cold junction (blue □'s), maximum temperature (black O's), (bottom) temperature difference as functions of incident laser power, (c) effective Seebeck coefficient, (d) inputted longitudinal (red X's) and perpendicular (blue O's) CNT thermal conductivity as functions of average temperature
Figure 39: Model 2 (a) induced voltage difference from simulation (red X's) and experiment (blue O's), (b) (top) hot junction (red X's), cold junction (blue □'s), maximum temperature (black O's), (bottom) temperature difference as functions of incident laser power, (c) effective Seebeck coefficient, (d) inputted longitudinal (red X's) and perpendicular (blue O's) CNT thermal conductivity as functions of average temperature

Figure 40: Model 3 (a) induced voltage difference from simulation (red X's) and experiment (blue O's), (b) (top) hot junction (red X's), cold junction (blue $\Box$ 's), maximum temperature (black O's), (bottom) temperature difference as functions of incident laser power, (c) effective Seebeck coefficient, (d) tuned longitudinal (red X's) and perpendicular (blue O's) CNT thermal conductivity as functions of average temperature
Figure 41: Model 4 (a) induced voltage difference from simulation (red X's) and experiment (blue O's), (b) (top) hot junction (red X's), cold junction (blue $\Box$ 's), maximum temperature (black O's), (bottom) temperature difference as functions of incident laser power, (c) effective Seebeck coefficient, (d) tuned longitudinal (red X's) and perpendicular (blue O's) CNT thermal conductivity as functions of average temperature
Figure 42: Time-dependent Model 4 temperature difference across (a) copper, (b) silicon, CNT, and entire device, induced voltage difference across (c) copper, (d) silicon, CNT, and entire device under incident laser power of $Q_0 = 337.5$ mW
Figure 43: Time-dependent Model 4 (a) temperature difference across silicon, CNT, and entire device, (b) induced voltage difference across silicon, CNT, and entire device under incident laser power of $Q_0 = 337.5$ mW
Figure 44: Time-dependent Model 4 (a, b) net temperature difference across entire device, (c, d) net induced voltage difference across entire device with varying incident laser power $Q_0$
Figure 45: Steady-state Model 4 induced voltage difference under incident laser power of $Q_0 = 337.5 \text{ mW}$ aimed at varying (left) x-coordinates and (right) y-coordinates, where the green star indicates the experimental coordinate
Figure 46: Perpendicular conduction device schematic sketched in 3D
Figure 47: Model 5 (left) surface temperature and (right) surface potential under incident laser power of $Q_0 = 283.5 \text{ mW}$
Figure 48: Model 5 temperature along z-axis through front ITO (solid red line), through the CNT forest (dashed green line), and through back ITO (dotted blue line) under incident laser power of $Q_0 = 283.5$ mW aimed at absolute centre of CNT sidewall
Figure 49: Model 5 (a) induced voltage difference from simulation (red X's) and experiment (blue O's), (b) (top) hot junction (red X's), cold junction (blue □'s), maximum temperature (black O's), (bottom) temperature difference as functions of incident laser power, (c) effective Seebeck coefficient, (d) input longitudinal (red X's) and perpendicular (blue O's) CNT thermal conductivity as functions of average temperature
Figure 50: Steady-state Model 5 induced voltage difference under incident laser power of $Q_0 = 283.5 \text{ mW}$ aimed at varying (left) x-coordinates and (right) y-coordinates, where the green star indicates the experimental coordinate
Figure 51: Model 5 (a) induced voltage difference from simulation with silicon substrate (red X's), with quartz substrate (green $\Box$ 's), without a substrate (blue O's), from experiment with silicon substrate (black $\diamond$ 's) as functions of incident laser power, (b-d) (top) hot junction (red X's), cold junction (blue $\Box$ 's), maximum temperature (black O's), (bottom) temperature difference as functions of incident laser power with silicon substrate, with quartz substrate, and without a substrate
Figure 52: Model 5 temperature along (a) X, (b) Y, (c) Z with CNT, silicon, and ITO (solid red line), CNT and ITO (dotted green line), CNT and Si (dot-dashed blue line), no silicon and ITO (dashed black line) under incident laser power of $Q_0 = 283.5 \text{ mW}$
Figure 53: Model 5 induced voltage difference from simulation (coloured O's) and from experiment

Figure 54: Model 5 temperature along Z with (a) CNT, silicon, and ITO, (b) CNT and ITO, (c) CNT and	l
Si under incident laser power of $Q_0 = 283.5$ mW with varied $\kappa_{CNT}$ , (d) temperature difference along Z as	a
function of $\kappa_{CNT}$ for all three configurations	2

# List of Symbols and Constants

Variable Symbol	Description	Unit or Value
Α	Cross-sectional area	m <sup>2</sup>
$A_c$	Absorption coefficient	cm <sup>-1</sup>
D	Thermal diffusivity	$m^2 \cdot s^{-1}$
$E_g$	Bandgap	J or eV
$\int_{0}^{\infty}$	Focal length	m
F	Geometric calibration factor (4-point probe)	(dimensionless)
h	Heat transfer coefficient	$W \cdot m^{-2}$
Ι	Current	Α
l	Mean free path	m
$k_B$	Boltzmann constant	$1.38 \times 10-23 \text{ m}^2 \cdot \text{kg} \cdot \text{s}^{-2} \cdot \text{K}^{-1}$
$M^2$	Laser beam quality spatial characteristic	(dimensionless)
L	Length	m
n	Electron density	cm <sup>-3</sup>
n	Refractive index	(dimensionless)
$N_L$	Lorenz number	$2.44 \times 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2}$
r	Thermal resistance	$K \cdot W^{-1}$
$r_{x}, r_{y}, r_{0}$	Radius (x, y, original)	m
R	Electrical resistance	Ω
$R_c$	Reflection coefficient	(dimensionless)
$R^2$	Coefficient of determination	(dimensionless)
S	Interprobe spacing (4-point probe)	m
t	Time	S
$t_h$	Thickness	m
Т	Absolute temperature	K
$T_P$	Power transmission coefficient	(dimensionless)
V	Voltage	V
W	Width	m
Ζ	Figure-of-merit	K-1
ZT	Dimensionless figure-of-merit	(dimensionless)
α	Seebeck coefficient (thermopower)	$\mathbf{V} \cdot \mathbf{K}^{-1}$
ε <sub>0</sub>	Permittivity of vacuum	$8.854 \text{x} 10^{-12} \text{ F} \cdot \text{m}^{-1}$
ε <sub>r</sub>	Relative permittivity	(dimensionless)
η	Efficiency	%
$\theta_{1/2}$	Half-divergence angle	rad
κ	Thermal conductivity	$W \cdot m^{-1} \cdot K^{-1}$
λ	Wavelength	m
П	Peltier coefficient	V
ρ	Electrical resistivity	Ω·m
σ	Electrical conductivity	$\mathbf{S} \cdot \mathbf{m}^{-1}$ or $\mathbf{\Omega}^{-1} \cdot \mathbf{m}^{-1}$
τ	Thomson coefficient	$\mathbf{V} \cdot \mathbf{K}^{-1}$
$\tau_c$	RC time constant (charging)	S
$ au_d$	RC time constant (discharge)	S

#### General Table of Symbols and Constants

Variable Symbol	Description	Unit or Value
$c_p$	Specific heat capacity at constant pressure	$J \cdot kg^{-1} \cdot K^{-1}$
n	Normal vector	(dimensionless)
q	Heat flux by conduction	$W \cdot m^{-2}$
Q	Volumetric heat source (or heat sink)	$W \cdot m^{-3}$
$Q_0$	Incident heat (laser) power	W
$Q_{SP}$	Setpoint heat (laser) power	W
Tamb	Ambient temperature	Κ
и	Velocity field vector	$\mathbf{m} \cdot \mathbf{s}^{-1}$
U	Internal energy	J
3	Surface emissivity	(dimensionless)
$\rho_d$	Volumetric mass density	kg⋅m <sup>-3</sup>
$\sigma_{SB}$	Stefan-Boltzmann constant	$5.670 \times 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$

COMSOL Heat Transfer Module Working Variables

COMSOL	AC/DC	Module	Working	Variables
0011002	110/20	1120000000		1 001 0000 000

Variable Symbol	Description	Unit or Value
В	Magnetic flux density	Т
D	Electric displacement or electric flux density	$\mathbf{C} \cdot \mathbf{m}^{-2}$
Ε	Electric field strength	$V \cdot m^{-1}$
Н	Magnetic field strength	$A \cdot m^{-1}$
J	Electric current density	$A \cdot m^{-2}$
$J_e$	External current density	$A \cdot m^{-2}$
Qj	Distributed current source	$A \cdot m^{-3}$
u	Velocity field vector	$\mathbf{m} \cdot \mathbf{s}^{-1}$
ρ	Electric charge density	$\mathbf{C} \cdot \mathbf{m}^{-3}$

# List of Abbreviations

AIREBO	Adaptive intermolecular reactive empirical bond order
APCVD	Atmospheric-pressure chemical vapour deposition
CNT	Carbon nanotube
CVD	Chemical vapour deposition
DSC	Differential scanning calorimetry
EMF	Electromotive force
FWCNT	Few-walled carbon nanotube
GPIB	General purpose interface bus
ITO	Indium tin oxide
LFA	Laser flash apparatus
LPCVD	Low-pressure chemical vapour deposition
MFC	Mass flow controller
MWCNT	Multi-walled carbon nanotube
PECVD	Plasma-enhanced chemical vapour deposition
PEEK	Polyether ether ketone
PPMS	Physical property measurement system
REBO	Reactive empirical bond order
SEM	Scanning electron microscopy
SWCNT	Single-walled carbon nanotube
TEC	Thermionic energy conversion
TEG	Thermoelectric generator
TEM	Transmission electron microscopy
TCO	Transparent conductive oxide
UHV	Ultra-high vacuum

## Acknowledgements

I would sincerely like to thank my supervisor, Professor Alireza Nojeh, for his support, guidance, and advice throughout this project, as well as for reviewing this thesis. I would also like to thank my colleague Mr. Andrew Koch and summer student Mr. Naser Janatipour for their contributions towards optimizing the chemical vapour deposition apparatus, as well as Dr. Mehran Vahdani Moghaddam for providing tall CNT forest samples greater than 1 mm in height. I would also like to thank my colleagues Mr. Amir Hossein Khoshaman and Mr. Mike Chang for their scanning electron microscope images presented here. Lastly, I would like to thank Professor Karen Kavanagh at Simon Fraser University for her transmission electron microscope images of the carbon nanotube forests.

# Dedication

To my parents.

## Chapter 1 – Introduction

#### 1.1. Motivation

Industrial waste heat is an inevitable by-product of industrial processes and can take the form of hot gases evacuated to the atmosphere, finished products with residual heat leaving the industrial process, or heat transferred off of hot equipment surfaces. According to the United States Department of Energy, as much as 50% of the energy consumed by manufacturing processes ends up as waste heat in the form of hot gases or liquids, and in the form of heat conduction, convection, and radiation from hot equipment surfaces [1]. Recovering waste heat has the potential to lower industrial operating costs by reusing the heat for preheating gases or furnace loads, space heating, or generating usable electrical energy. All at the same time, this has the benefit of reducing the industry's ecological footprint.

Thankfully, two forms of heat recovery technologies are already in practice. In the case of industrial power plants, *heat engines* take advantage of the Rankine cycle. This uses the phase change of an operating fluid (e.g. water to steam) to drive a turbine and generate electrical energy. The organic Rankine cycle uses the same working principle, but uses organic fluids with high molecular masses and low boiling points so that lower temperature waste heat can be recaptured. The problem with this technology is that electric energy is recaptured using machinery with moving parts that are subject to wear and tear. The other form, the *thermoelectric effect*, uses either a pair of dissimilar metals or a semiconducting p-n junction. Thermoelectric devices allow for the direct conversion of heat, which could originate from lower grade (lower temperature, under 100 °C) solar energy, geothermal energy, or waste heat, and into usable electrical power. Because there are no moving parts, its advantage over heat engines is a lower maintenance requirement, zero noise operation if using heat sinks, and a higher modularity. Although at higher temperatures the Carnot efficiency of a heat engine is improved, the mechanical parts could fail more easily and lubricants can reach their dangerous flash point temperatures. This is again where thermoelectric devices have an advantage.

With the onset of sensor and actuator technologies, the need for regenerative and decentralized small power sources has risen. For example, NASA's Voyager and Cassini missions already utilize the Seebeck effect (direct conversion of heat to electricity) in their radioisotope thermoelectric generators (TEGs) [2]. On a larger and more widespread scale, waste heat is also given off in the form of automotive engine or radiator heat, which can potentially be recaptured and reused. TEGs offer the ability to convert waste heat into microwatts to milliwatts of usable electrical energy, which could be sufficient to power a microcircuit.

#### 1.2. The Thermoelectric Effect

Parts of Chapters 1.2-1.5 have been adapted with permission from Khoshaman, et al. [3]. The simplest schematic of a thermoelectric device comprises of a segment of one metal (A) joined at both ends by two pieces of a different metal (B). The first of the thermoelectric effects was discovered by Seebeck, who showed that if the two junctions between metals A and B are held at different temperatures ( $\Delta T = T_H - T_C = T_2 - T_I$ ), an open-circuit electromotive force (EMF) is produced at the two free ends of metal B ( $\Delta V = V_H - V_C$ ), which are held at the same temperature ( $T_0$ ). The voltage developed follows Equation (1-1) and is schematically shown in Figure 1 below. When one of the junctions is heated, electrons are able to surmount the potential energy barrier and travel from the material in which they have lower energy and into the material in which they have higher energy, and this leads to an electromotive force in the load. This is the Seebeck effect or the power generation mode. The appropriately named differential Seebeck coefficient (also known as the thermopower) is shown below in Equation (1-2) and has units of V/K. The Seebeck coefficient is typically in the ones to tens of  $\mu V/K$  for metals and tens to hundreds for semiconductors. By convention, the coefficient is positive if the electromotive force drives an electric current through conductor A from the hot to the cold junction [4]. The Seebeck coefficient represents the magnitude of the induced voltage as a result of a temperature difference across a material.

$$\Delta V = \int E \cdot dx = \int \alpha(T) \frac{dT}{dx} = \int_{T_0}^{T_1} \alpha_B(T) dT + \int_{T_1}^{T_2} \alpha_A(T) dT + \int_{T_2}^{T_0} \alpha_B(T) dT$$

$$\Delta V = \int_{T_1}^{T_2} \alpha_A(T) dT + \int_{T_2}^{T_1} \alpha_B(T) dT = \int_{T_1}^{T_2} (\alpha_A(T) - \alpha_B(T)) dT$$

$$\alpha_{AB}(T) = \frac{\Delta V}{\Delta T} = \frac{V_2 - V_1}{T_2 - T_1} = \alpha_B - \alpha_A$$
(1-2)



Figure 1: Schematic of Seebeck effect with metal A and B

The Seebeck effect is implemented in thermocouples to measure a temperature difference quantifiable by a voltage, and if calibrated correctly with a standard or reference, it can be used to measure the absolute temperature. By applying a temperature difference across a thermocouple, charge carriers are forced to diffuse from the hot to the cold side, creating a net buildup of charge carriers or an electric potential. A further increase in the temperature difference would continue to build up more charge carriers on the cold side and, therefore, continue to induce a larger thermoelectric voltage.

The related, but opposite thermoelectric effect was later discovered by Peltier using the same device schematic as Seebeck's. By applying an external electromotive force to the two free ends of metal B, an electric current (I) causes a heating at one junction (+Q) and a cooling at the other junction (-Q). As current travels from one metal into a different metal, the potential energy of the electrons becomes altered, and this results in either a heating or cooling, depending on the direction of current flow. The Peltier effect or refrigeration is defined by the Peltier coefficient ( $\Pi$ ) as:

$$\Pi_{AB} = \frac{Q}{I} \tag{1-3}$$

, with units of W/A or V. By convention, the Peltier coefficient is positive if the junction where current enters metal A is heated and the junction where current leaves metal A is cooled [4].

Shortly after, Thomson (Lord Kelvin) realized that the Seebeck and Peltier effects are dependent on one another and can be defined by the Thomson relations, as shown below in Equations (1-4) and (1-5). He also realized that there is reversible heating or cooling in homogeneous conductors when there is both a flow of current and a temperature gradient. The Thomson coefficient ( $\tau$ ) is the rate of heating per unit length per unit temperature resulting from passing a unit of current along a conductor where there is a temperature gradient.

$$\Pi_{AB} = \alpha_{AB}T \tag{1-4}$$

$$\tau = T \frac{d\alpha}{dT} \tag{1-5}$$

The majority of commercially-available thermoelectric devices comprise of an array of thermocouples arranged electrically in series and thermally in parallel, sandwiched between a thermally conductive (and electrically insulative) hot and cold plate. Each individual thermocouple is made up of a semiconducting p-type leg and an n-type leg, since  $\alpha$  is positive in p-type materials and negative in n-type materials. A schematic of a single p-n thermocouple is shown below in Figure 2 (© 2014 IEEE, with permission from Khoshaman, et al. [3].) for both power generation (Seebeck) on the left and refrigeration (Peltier) on the right. A single thermocouple is capable of producing tens to hundreds of  $\mu$ V per degree of temperature

difference, so this is why many elements are required to generate the operating voltage of transistors for electronic applications, for example.

The current commercially available thermoelectric materials are split into three categories, depending on the operating temperature range. Bismuth (Bi) alloys with antimony (Sb), tellurium (Te), and selenium (Se) are low temperature (up to 450 K) and are typically used in Peltier refrigeration. Lead telluride (PbTe) devices are intermediate temperature (up to 850 K). Silicon germanium (SiGe) alloys are high temperature (up to 1,300 K) [5].



Figure 2: Schematic diagram of (left) Seebeck power generation device and (right) Peltier refrigeration device, © 2014 IEEE, with permission from Khoshaman, et al. [3]

### 1.3. Quantifying the Performance of the Thermoelectric Effect

The thermoelectric effects themselves are thermodynamically reversible. However, practical devices always contain some form of electrical resistance and thermal conduction losses. The performance of a thermoelectric device can be quantified as a function of the Seebeck coefficient and the electrical and thermal conductivities of the two connected materials. For optimal performance, there needs to be a pair of materials with high electrical conductivities to allow for easy passage of charge and low thermal conductivities to enable the device to operate under high temperature gradients. The dimensionless figure-of-merit for a single thermoelectric material can therefore be defined as:

$$ZT = \frac{\alpha^2 \sigma T}{\kappa} \tag{1-6}$$

, where  $\alpha$  is the Seebeck coefficient,  $\sigma$  is the electrical conductivity, *T* is the absolute temperature in Kelvin, and  $\kappa$  is the thermal conductivity. The efficiency of thermoelectric power generation device (Seebeck effect) is defined as the ratio of energy supplied to the load to the heat energy input, which can be shown to be equal to [6]:

$$\eta = \frac{T_H - T_C}{T_H} \frac{\sqrt{1 + ZT_m} - 1}{\sqrt{1 + ZT_m} + \frac{T_C}{T_H}} = \eta_{Carnot} \frac{\sqrt{1 + ZT_m} - 1}{\sqrt{1 + ZT_m} + \frac{T_C}{T_H}}$$
(1-7)

, where  $T_H$  and  $T_C$  are the hot- and cold-side temperatures and  $T_m$  is the average of the two temperatures. It can be seen that by increasing *ZT*, the device efficiency can approach the theoretical Carnot efficiency. In an ideal and reversible Carnot cycle, input heat at a higher temperature is rejected at lower temperature, and since not all the heat can be used to do work in a heat engine (Second Law of Thermodynamics), the Carnot efficiency places this upper limit.

Figure 3 below shows a plot of efficiency versus  $ZT_m$  for increasing values of temperature differences, assuming a cold side temperature of 300 K. For a given  $ZT_m$ , as the temperature gradient is increased, the device efficiency is also increased.



Figure 3: Power generation efficiency vs.  $ZT_m$  at varying  $T_{hot}$ 

Unfortunately, the efficiency ( $\eta$ ) of thermoelectric generators based on bulk materials is still intrinsically low. In classical bulk thermoelectric materials, the three components of the figure-of-merit (*Z*) are interdependent on one another. The numerator of *Z*, also known as the power factor, is mostly dominated by charge carriers. The denominator, which is just the thermal conductivity, is mostly dominated by heat conduction by acoustic phonons in semiconductors [7] and by electrons in metals.

Unfortunately, there is an impeding optimization of the three components of Z. An increased electron density (*n*) results in an increased electrical conductivity  $\sigma$ , but a decreased Seebeck coefficient ( $\alpha$ ). Electrical conductivity can also be increased through a longer electron mean free path ( $l_e$ ) and this does not decrease the Seebeck coefficient. However, crystals with low defects are usually required, which implies a longer phonon mean free path ( $l_{ph}$ ) and consequently an increased thermal conductivity ( $\kappa$ ), which is undesirable. Thermal conductivity contains components of heat transfer through contributions by electrons

 $(\kappa_{el})$  and by phonons  $(\kappa_{ph})$ , where both should be suppressed as much as possible. The Wiedemann-Franz Law  $(\kappa_{el} = \sigma N_L T)$ , where  $N_L$  is the Lorenz number and T is the temperature, states that there is a trade-off in optimizing ZT since any desirable reduction in  $\kappa_{el}$  would result in an undesirable reduction in  $\sigma$ . Through quantum confinement,  $\kappa_{el}$  can be controlled and minimized. However, reducing  $\kappa_{ph}$  is a challenging task, since phonon heat flow from the hot to the cold junction contributes to reducing the temperature gradient.

Historically, the thermoelectric effect was discovered and studied in metals since metals were the only conductors properly known at the time. Unfortunately, all metals exhibited *ZT* values much less than 1 for all temperatures. Ioffe showed that by using the free electron gas model and varying the electron density, there exists a maximum in the *Z* vs. *n* curve in the region around  $n = 10^{19}$  cm<sup>-3</sup>, which is in the regime of doped semiconductors [8]. The power factor of *Z* can be optimized in narrow-bandgap ( $E_g \approx 10k_BT$ ) doped semiconductors [7]. The bandgap needs to also be sufficiently large in order to minimize the minority carrier contributions to the overall Seebeck coefficient [9]. High mobility carriers are desirable in order to achieve the highest electrical conductivity for a given carrier concentration.

#### 1.4. Nanostructured Thermoelectrics

With the onset of semiconductor research in the mid-1900's, thermoelectric devices using semiconductor materials proved to be more practical due to their enhanced thermoelectric properties. With that being said, nanostructured materials can potentially offer a method for optimizing the *ZT* through effects such as quantum confinement, modulation doping, and an increased influence from nano-interfaces and nano-surfaces [10]. For example, a figure-of-merit greater than 1 has been observed in PbSeTe-based quantum dot superlattices [11] and as high as 2.4 has been observed in Bi<sub>2</sub>Te<sub>3</sub>/Sb<sub>2</sub>Te<sub>3</sub> superlattices [12]. Most recently, a record high *ZT* of 2.6 at 923 K has been measured along the *b*-axis of the room temperature orthorhombic unit cell of SnSe crystals [13].

Low-dimensional nanostructured materials (2D quantum wells, 1D quantum wires, or 0D quantum dots) can be tailored to modify the interdependence of the three parameters quantifying the figure-of-merit through two mechanisms: increasing the power factor through size quantization, and decreasing the lattice thermal conductivity through boundary phonon scattering [7]. We can first define *L* as the relevant length scale in low-dimensional solids (2D well width, 1D wire diameter, 0D dot diameter). Through two important realizations, *L* can be taken advantage of. Firstly, in the regime of diffusive transport,  $\sigma$  is determined by the electron mean free path ( $l_e$ ), and  $\kappa_{ph}$  (phonon component of thermal conductivity) is determined by the phonon mean free path ( $l_{ph}$ ). Low-dimensional thermoelectric devices should be fabricated with length scales *L* that limit  $l_{ph}$ , but not  $l_e$  [7]. As a result, this can potentially reduce  $\kappa$  without decreasing  $\sigma$ . Secondly, size-quantization effects have the potential to increase  $\alpha$  without affecting the charge carrier density and  $\sigma$ . The Seebeck coefficient is enhanced because it is a function of the energy

derivative of the electron density of states, which becomes more sharply peaked in lower dimensional materials. However, the system must be free from disorder as much as possible so that the band structure model holds true. Especially in small L nanostructures, there can be a high possibility that defects can localize the electron wavefunction to one region of the device and impede electron transport.

#### 1.5. Carbon Nanotube-Based Thermoelectrics

Carbon nanotubes (CNTs) have gained widespread attention in the research community. Due to their chemical stability, flexibility, strong mechanical properties, and superior electric properties, they are on the path of becoming promising candidates for use in new types of electronic devices. The simplest CNT is a single sp<sup>2</sup>-bonded sheet of graphene rolled into a seamless cylinder and stabilized by van der Waals intermolecular forces. This is appropriately named a single-walled carbon nanotube (SWCNT). A SWCNT can exhibit either metallic or semiconducting properties depending on its chirality. Multiple graphene sheets can be rolled and concentrically aligned to form a multi-walled carbon nanotube (MWCNT), which is always metallic. The electronic properties of CNTs are not only sensitive to intrinsic properties, namely the number of tubes, the chirality, and diameter, but also the extrinsic properties, such as defects, doping, and the external environment. Carbon nanotubes are in essence a 1D material due to their very high aspect ratio, and low-dimensional materials have been previously mentioned to have superior thermoelectric properties compared with their bulk counterparts.

Although experimental studies on single-walled and multi-walled carbon nanotubes in bulk sheet or vertically-aligned forest form have reported electrical conductivities as high as in the  $10^3 - 10^4$  S/m range, Seebeck coefficients remain on the relatively low side in the  $10 - 50 \mu$ V/K range [14-17]. Thermal conductivity has been shown to be more sensitive to the sample geometry, namely whether measuring a single tube, a bundle, or a film. Also, there is a strong influence of the nanotube chirality [18-20] and length [19, 21, 22] on the thermal conductivity. Experimental reports have shown thermal conductivity to vary extremely widely, in the  $1 - 10^4$  W·m<sup>-1</sup>·K<sup>-1</sup> range [23]. In the best case scenario, the room temperature *ZT* value has been measured to be as high as  $10^{-3}$  for DWCNT bundles [24], MWCNT powders [14], CNT sheets or papers [16, 25], or composites with polymers [26-28]. This is still a few orders of magnitude less than well-established materials, such as the previously mentioned alloys of bismuth, lead-telluride, or silicon-germanium. CNTs on their own are not the ideal choice for thermoelectric applications due to their relatively low figure-of-merit and consequently low efficiency. However, CNTs can be fabricated from the world's many abundant carbon-containing derivatives at very low costs, which can potentially offset the efficiency drawback. Also, since carbon has a very low atomic mass of 12 amu, carbon-based thermoelectric devices can be a promising solution where a high power-to-weight ratio is desired.

### 1.6. The "Heat Trap" effect

One method to locally heat a material is by illuminating it with a beam of light. For example, this could be performed with focussed light from the sun or from visible or infrared lasers in the lab. In practice, localized heating is relatively straightforward to accomplish with insulators. However, much higher powers of incident light are required to heat a metal to the same temperature. This is because metals do an excellent job of dissipating the incoming heat to its surroundings, owing to their high thermal conductivities.

However, forests of CNTs are known to be strong absorbers of light and similar to an ideal black body [29]. It has been shown experimentally that when a forest of multi-walled CNTs under modest- to high-vacuum is heated by a low-power visible laser, the heat from the focussed laser is allowed to dissipate longitudinally along the length of the nanotubes, and to a much less extent, radially or axially between nanotubes. The temperature of the CNT at the heated spot slowly rises as one would expect. However, beyond a certain laser intensity (threshold), the rate of heat generation surpasses that of the rate of heat dissipation [30]. The result is a significant rise in heating at the laser spot, a quick rise in temperature, and a reduction in thermal conductivity of that region, leading to the localization of heat to the illuminated spot. As well, a bright and localized incandescent glow approximately the size of the laser beam spot becomes visible on the sidewall of the CNT forest. This isolated and effective positive-feedback heating effect was named the "Heat Trap" effect [30].

From molecular dynamics simulations reported in the literature, the longitudinal thermal conductivity of a SWCNT (along its axis) at room temperature has been shown to be as large as that of diamond or graphite [18, 19, 31] due to strong intermolecular bonds. However, the perpendicular thermal conductivity (radially or axially) between nanotubes is much lower due to weak tube-tube van der Waals coupling interactions [32], where one study has shown the perpendicular conductivity being as much as two orders of magnitude smaller than the longitudinal conductivity [33]. At temperatures higher than room temperature (up to 800K), the simulated and experimental thermal conductivity of an individual SWCNT has been shown to follow a 1/T dependence due to Umklapp phonon-phonon scattering [31, 34-36] and a  $1/(\alpha T + \beta T^2)$  due to second-order three-phonon scattering [36] respectively. Although these trends were reported for an individual SWCNT, the experimental "Heat Trap" effect in forests of MWCNTs has been explained based on the very same fall-off in thermal conductivity at elevated temperatures.

Two intrinsic properties of CNTs can be taken advantage of if they are to be used as one material in a thermoelectric device. Firstly, we know that there exists a fall-off in thermal conductivity at working temperatures beyond the threshold for "Heat Trap" conditions. As a result, the region on a CNT forest that is heated (by ~50 W/cm<sup>2</sup> laser) acts as a poor thermal conductor and reaches a temperature gradient as high as 1,200 K/mm [37]. A bulk isotropic conductor in comparison would require over three orders of

magnitude higher incident light intensity to achieve the same temperature. Therefore, a localized and hightemperature confined pocket of heat can thus be created. Secondly, due to the 1D nature of CNTs, the thermal conductivity of a CNT forest is highly anisotropic. The majority of heat dissipation happens along the nanotube axes, rather than perpendicularly between nanotubes. A thermoelectric device using CNTs should be constructed in such manner to maximize the temperature gradient between two junctions if one wishes to optimize the device efficiency. Therefore, due to these aforementioned properties of carbon nanotubes, CNTs can potentially be excellent candidates for thermoelectric energy conversion devices.

### 1.7. Comparison with Thermionic Energy Conversion

Thermionic energy conversion (TEC) is another process that involves the conversion of heat to electricity (or light to heat to electricity) and has been studied for over a century. In a TEC device under operation, electrons are thermionically emitted from the hot electrode (emitter or cathode) into vacuum. The electrons then traverse the interelectrode distance, and with sufficient kinetic energy, eventually are collected at the cold electrode (collector or anode). Eventually, a negative charge builds up at the anode and hinders further electron collection; a zero net electron flux. A circuit could be connected to the two electrodes, whereby electrons will flow through the load and back into the emitter, generating a steady-state output voltage and current.

Thermoelectric energy generation is in essence quite similar to thermionic energy conversion, but without an interelectrode gap. Therefore, a TEG has the advantage of not necessarily having to be operated under vacuum (with the exception of the "Heat Trap" effect) and thus simplifying device prototyping. TEGs have the advantage that electrical energy can be generated as long as there is a temperature difference between the two junctions of dissimilar metals. TEC requires extreme temperatures in excess of 1000 °C to "boil" electrons off the surface of the cathode (unless the cathode has an extremely low work function). Therefore, TEGs can potentially be used to recapture low-grade or low-temperature waste heat in places where TECs cannot. However, this comes at the price of a relatively lower efficiency compared with thermionics.

### 1.8. Objectives

The use of light to induce a thermoelectric voltage in carbon nanotubes has been previously reported in the literature for a few applications. Devices based on the photo-thermoelectric effect of SWCNT sheets include visible light detectors [38, 39], infrared detectors [40], p-n junction photodetectors [41, 42], and field-effect transistors [43]. Pressed pellets of polyaniline with SWCNTs or MWCNTs have been studied for their thermal diffusivity and thermal conductivity [44, 45]. Other devices include a position-sensitive freestanding SWCNT film thermoelectric device [46]. Another device has been created using bismuth-based thin films coated with a SWCNT light-absorption layer, where ultraviolet to near-infrared lasers can

induce an open-circuit voltage [47, 48]. Similarly, a novel photo-thermal hydrogel-CNT composite layer has been deposited onto the hot interface of a bismuth-telluride module, where near-infrared laser radiation can induce a photo-exothermic response [49, 50].

With regards to MWCNTs, the anisotropic thermal diffusivity [51-53] and thermal conductivity [54] has been measured using the photo-thermoelectric effect. Upon laser irradiation, a thermal wave is first produced in the sample and is detected using a fast thermoelectric effect at the junction between the sample and a sharp probe.

However, to our knowledge, a device capable of producing a thermoelectric voltage by light irradiation on a forest of aligned multi-walled carbon nanotubes has not yet been reported in the literature. The primary objective of this project was to study the thermoelectric effect for energy generation using carbon nanotube forests as the core material in a thermocouple arrangement. In this work, CNT forests were first characterized in ambient conditions using direct heating, and then the fabricated devices were then evaluated in vacuum using laser heating. Two novel thermoelectric devices were built based on two intrinsic properties of CNT forests: firstly, the "Heat trap" effect, involving the localization of light-induced heat and, secondly, the highly anisotropic thermal conductivity of CNTs. Both CNT material properties are beneficial towards enhancing the figure-of-merit and the device efficiency. A finite element analysis model was also created to simulate the thermal, electrical and thermoelectric properties of the fabricated devices. The temperature-dependent thermal conductivity of CNTs was derived based on the experimental induced voltage of the devices.

#### 1.9. Thesis Outline

At first, Chapter 2 provides a description of all the equipment and apparatuses that were used and optimized towards growing carbon nanotube forests in the lab. The nanotubes grown by the method described in this chapter were used to fabricate the thermoelectric devices used and tested in the following chapters. Chapter 3 describes the theory and methodology behind how the three relevant parameters necessary to quantify a thermoelectric device's figure-of-merit and device efficiency are measured, which are the Seebeck coefficient, the electrical conductivity, and the thermal conductivity. Chapter 4 is dedicated to the experimental results of measuring the Seebeck coefficient and thermoelectric performance in ambient conditions, and the photo-voltages of the two novel devices in vacuum using various sample holders. Lastly, Chapter 5 introduces the theory behind the thermal and electrical physics modules used in the finite element analysis software, then describes a number of simulated models with increasing complexity. Both devices are modelled, where the thermal conductivity of CNTs is derived from experimental photo-voltages.

## Chapter 2 – Carbon Nanotube Fabrication

#### 2.1. Introduction

CNTs are commonly "grown" by catalytic chemical vapour deposition (CVD). For CVD growth, a hydrocarbon vapour is first thermally dissociated (pyrolysis). Incoming vapour carbon species dissolve into the hot metal nanoparticle catalysts lying on a substrate, which is typically a silicon wafer, but can also be quartz. After surpassing the carbon-solubility limit of the metal, which is temperature-dependent, carbon species begin to precipitate and crystallize outwards in a cylindrical network (nanotube) without forming any dangling bonds [55].

### 2.2. CNT Growth

In the early stages of nanotube research, it was proposed by Smalley *et al.* that new carbon atoms could be added directly onto an open edge of a growing (10,10) SWCNT. This was coined the "scooter mechanism" [56], whereby the chemisorbed metal nanoparticles "scoot" around the nanotube open edge and keep the tube end open. This mechanism suggests that as the metal nanoparticles zip around, they catalytically anneal any defects and re-arrange pentagons into hexagons, thus increasing the nanotube length. Doing so, the metal nanoparticles inhibit fullerene or nanotube closure and termination by partially terminating the dangling bonds and exchanging spots with the incoming carbon species [57]. However, once the metal nanoparticles have reached a critical size, they get detached from the tube or become saturated with carbon, and the growth is terminated.

There are two other possible and well-accepted growth mechanisms that help explain the precipitation of CNTs [55]. In the first case, if the substrate-catalyst interaction energy is weak, the metal nanoparticles form acute contact angles with the substrate. Incoming carbon species diffuse from the top surface of the metal nanoparticles down towards the substrate. CNTs precipitate downwards and lift the metal nanoparticles up and away from the substrate. This is the "tip-growth" method which raises the catalyst nanoparticles upwards. If the tops of the metal nanoparticles are exposed and the metal isn't yet fully saturated with carbon, then the CNT will grow longer and longer. The catalytic activity of the metal slows down and eventually stops once the metal nanoparticles have been completely covered and saturated with carbon species. At this point, growth also stops.

In the other method, the substrate-catalyst interaction energy is strong and the metal nanoparticles form obtuse contact angles with the substrate. Just like before, carbon species diffuse into the annealed and reduced metal nanoparticles and a graphene cap on the catalyst is formed. However, this time, CNTs cannot push the metal nanoparticles up, so CNTs precipitate out from the top surface of the nanoparticles emerging from the metal's apex. Growth begins as a carbon-containing hemispherical dome. Further carbon species diffusing at the lower peripheries of the catalyst are added into the network, which extends upwards into a seamless graphitic cylinder. This is the "root-growth" or "base-growth" method, which leaves the catalyst nanoparticles attached to the substrate.

The growth of both single-walled and multi-walled nanotubes can occur by these methods. It has been suggested that the size of the nanoparticle catalyst determines the size of the graphitic "filament," whereby as the diameter of the metal particle is decreased, the filament curvature is increased, which places a strain on the basal planes of the crystallites [58, 59]. The energetically-favourable and continuous shape of a MWCNT is formed. As the diameter is decreased even more, SWCNTs are formed. It has been experimentally shown by one study that SWCNT to FWCNT (few-walled carbon nanotube, < 7 walls) structures less than 5 nm in diameter grew by "root growth" from small cobalt, iron, or nickel nanoparticle catalysts also less than 5 nm in diameter [60]. Conversely, it was also shown that MWCNT structures greater than 15 nm in diameter grew by "tip-growth" from larger (> 15 nm diameter) nanoparticles of the same metals.

lijima has reported an astounding 96% empty space in the footprint of a SWCNT forest [61]. The low packing density of CNTs in "root-growth" mode is believed to be essential for carbon radicals to arrive at the catalyst/CNT interface at the substrate [62]. On the other hand, an excessively high packing density of CNTs would inhibit the diffusion of carbon radicals to the interface. In general, carbon species cannot penetrate to the bottom of the forests if the mean free path of the gas is much larger than the distance between nanotubes [63]. Also, an insufficiently high packing density would result in CNTs either not growing vertically and/or forming a lump or mat [61]. This would cover the catalyst and effectively cease growth. Therefore, in order to grow tall CNT forests, both the catalyst and growth conditions must be optimized.

The primary role of the catalyst is to decompose the hydrocarbon molecules at temperatures lower than that required for the spontaneous decomposition of the hydrocarbon. Typically, transition metals such as iron, cobalt, or nickel are used. It has been explained that the non-filled 3*d* orbitals in these transition metals overlap with those in the adsorbate hydrocarbon and favour the dissociation reaction [64]. There is electronic interaction between the "donor" adsorbate hydrocarbon and the "acceptor" metal. Compared with other transition metals, these three are considered to have higher adhesion with the growing CNT network and are more efficient in forming high-curvature (low-diameter) CNTs [65]. For the CNTs grown for this work, iron was chosen for its high carbon-solubility, high carbon-diffusion rate, high melting point, and low equilibrium vapour pressure [55], which works well for the temperatures required to dissociate carbon precursors (e.g. methane, ethylene, acetylene, benzene, xylene, or carbon monoxide). However, bulk iron

cannot catalyze the decomposition reaction of a hydrocarbon gas to form carbon filaments because it has to be dispersed. The iron layer deposited by electron-beam evaporation is a thin film. Annealing in the presence of argon and hydrogen allows the iron atoms to move to the most energetically favourable positions and to form nanoparticles [64]. In order to grow CNTs, rather than amorphous carbon, small diameter metal nanoparticles are required. Small diameters (< 5 nm) produce SWCNTs [66], large diameters (> 10 nm) produce MWCNTs, and medium diameters produce a mixture of the two [60, 67]. Hydrogen decomposition should only happen on the metal surface, and this can be controlled through fine-tuning the selection of the hydrocarbon source and its vapour pressure, choosing the right catalyst concentration, and optimizing the CVD reaction temperature [55].

To create a thin film of catalyst, I have deposited a 10 nm alumina buffer layer, followed by a 1 nm iron catalyst nucleation site layer under electron-beam evaporation ( $\pm 0.1$  nm) on a number of 4" diameter and 500 µm thick p-type ( $\rho = 0.001$ -0.005  $\Omega$ ·cm) silicon wafers. The alumina buffer layer prevents the formation of iron silicides at temperatures greater than 750 °C [68]. The wafers were then diced into "chips" approximately 6x6 mm<sup>2</sup> in footprint, whereby an isolated forest can be grown on each chip.

#### 2.3. Chemical Vapour Deposition Apparatus

In order to study carbon nanotube-based thermoelectric energy generation, an atmospheric-pressure chemical vapour deposition (APCVD) reaction apparatus was used to grow the CNTs. The in-house CVD apparatus was initially built by previous students [69], based on the designs by Hart *et al.* [70], and further improved and optimized by myself with assistance from my colleagues. It consists of a custom-designed quartz reaction vessel connected at the gas inlet by a 1" outer diameter graded quartz-to-metal junction, and at the exhaust outlet and electrical feedthrough by a 2" inner diameter custom-machined aluminum end cap. The gases used are argon (Ar, 5N, carrier), hydrogen (H<sub>2</sub>, 5N, carrier, reducing agent), and ethylene (C<sub>2</sub>H<sub>4</sub>, 2.5-5N, carbon precursor). Using Viton (inlet) and silicone (outlet) O-rings, the system is sealed from flammable gas leaks at atmospheric pressure. Figure 4 below illustrates the gas plumbing schematic, whereby optional components are shown in the dashed boxes. Ball flowmeters can optionally be installed downstream from the MFCs as a visual indication to the user that a gas is flowing. A roughing pump and pressure controller connected downstream from the CVD reaction vessel can be optionally installed to create a low-pressure CVD (LPCVD) apparatus.



At the inlet side of the CVD reactor, the quartz tube is heated by a digital tubular furnace to a constant 850 °C. This is designated as Zone 1 and can be seen in photo in Figure 5 below. Near the outlet side, a suspended silicon wafer (p-type,  $\rho = 0.001-0.005 \ \Omega \cdot cm$ ) heated platform is mechanically attached to the end cap and electrically connected via the electrically- and thermally-insulated electrical feedthrough. By passing a large constant current through the wafer, the wafer then undergoes resistive Joule heating and allows one to heat the substrate. This is designated as Zone 2 and shown in the left of Figure 8 below. The temperature at Zone 2 is typically held constant at 740-760 °C ±1 °C, which is measured by an Omega infrared thermometer. By using a 2-Zone setup, C<sub>2</sub>H<sub>4</sub> can first be activated (pyrolyzed) in Zone 1, whereby then traversing a relatively short residence distance towards Zone 2 ensures minimal "sooting" on the quartz sidewalls. Once the carbon radicals have reached Zone 2, the substrate heater has provided sufficient activation energy to the growth catalyst and has prepared the substrate for CNT growth. By decoupling the two processes at potentially different Zone temperatures, a higher level of growth control can be attained.



Figure 5: Photo of CVD apparatus in lab

## 2.4. Gas Flow Rate Calibration

Flows of argon, hydrogen, and ethylene gases can be controlled either manually by ball flow meters or electronically by analog MKS 1179a mass flow controllers (MFCs), the latter having a precision of  $\pm 1\%$  of full scale. A digital MFC has the advantage that it can be re-programmed for any gas, does not lose its calibration over time, and typically is more accurate and faster to achieve a setpoint than its analog counterparts. By first connecting the ball flow meters in series with a downstream digital Horiba SEC-N100 MFC with a precision of  $\pm 0.3\%$  of full scale, the flow meters can be calibrated to ensure correct flow rates and reproducibility. As seen below in Figure 6, the red X's represent the manufacturer's reported flow rates corresponding to the arbitrary flow meter scale, whereas the blue O's represent the actual flow rate measured by the digital MFC. Flow rates are well in agreement for argon shown in part (a). However, hydrogen and ethylene flow rates in parts (b) and (c) respectively diverge from their reported values by as much as 20% at maximum flow rate. From the blue O's in the plots below, calibrated look-up tables can be created for each gas.



Figure 6: Ball flow meter flow rates reported by (red X's) manufacturer and (blue O's) measured for (a) Ar, (b) H<sub>2</sub>, (c) C<sub>2</sub>H<sub>4</sub>

By then connecting the analog MFCs in series with a downstream digital MFC, the analog MFCs can also be calibrated. As seen below in parts (a) through (c) of Figure 7, the same three gases were calibrated through their respective analog MFCs. Although linear in this range, the flow rate setpoint entered into the MKS flow controller does not correspond to the actual measured flow rate. Therefore, a look-up table can be generated given the following relations, shown as Equations (2-1) to (2-3) below, where setpoint *SP* and desired flowrate *FR* are in units of sccm.

$$SP_{Ar} = (0.5101 * FR) - 10.28 \tag{2-1}$$

$$SP_{H_2} = (0.9981 * FR) + 5.62$$
 (2-2)

$$SP_{C_2H_4} = (0.9388 * FR) - 2.69 \tag{2-3}$$



Figure 7: Analog MKS MFC flow rates measured using digital MFC at varying setpoints for (a) Ar, (b) H<sub>2</sub>, (c) C<sub>2</sub>H<sub>4</sub>

### 2.5. CNT Growth Recipe

From a literature survey of MWCNT growth by APCVD, as shown below in Table 1, all growth parameters vary widely and appear to be specifically tuned to a given reaction vessel. Nevertheless, these parameters offer a good starting point towards developing our own growth recipe. For completeness, a similar literature survey was conducted for SWCNT growth by APCVD, as shown below in Table 2. Although the in-house CVD apparatus does not currently have the capability to grow SWCNTs, only a water bubbler and perhaps some additional process gases would be required. Smaller catalyst nanoparticles would need to be deposited onto the silicon substrates as well. A more systematic approach towards characterizing and calibrating the electron beam evaporator deposition of catalyst layers would need to be undertaken for such a task.

Catalyst Thickness (nm)		Process Gas Flow Rate (sccm)			Substrate Temperature (°C)	Growth Time (min)	Max Height (µm)	Ref.
Al <sub>2</sub> O <sub>3</sub>	Fe	Ar	$H_2$	$C_2H_4$				
10	1	100	400	115	810	15	1500	[70]
10	3	350	200	150	775	15-90	1500	[71]
2-20 (Al)	< 10	1000	0	1000	750	10	100	[72]
20	1.2	200	500	100	750	15-60	1000-2000	[73]
	?	?	0	1000	700	15-60	100-200	[74]
10	1	140	400	115	Up to 850	15	100-1000	[75]
10	1.2	600	400	150	770	15	650	[76]

Table 1: MWCNT growth parameters from the literature

Table 2:	<b>SWCNT</b>	growth	parameters	from	the	literature
1 000 00 11	0110111	0.01111	per en en er	<i>j. o</i>		

Catalyst Thickness (nm)		Process Gas Flow Rate (sccm)			Other Process Gases		Substrate Temp. (°C)	Growth Time (min)	Max Height (µm)	Ref.
Al <sub>2</sub> O <sub>3</sub>	Fe	Ar	$H_2$	$C_2H_4$	He	H <sub>2</sub> O Vapour				
1.5	10	1300		100		80 sccm	750	?	100-500	[62]
40	0.8-3	0	900	100	1000	100 ppm	755	10	Thin film	[77]
10	1	0	80	15	120	150-500 ppm	810	30 min- 12 hrs	7000	[78]
1.2	10	100	500	200		(99% Ar /1% O <sub>2</sub> )	750	30-135	2000- 5000	[79]
35	?	0	1000 (with He)	100		100-150 ppm	750	10	1500	[80]

The following growth recipe has been optimized by myself with assistance from my colleagues. From a cold-start, Zone 1 is heated up to 850 °C and the current delivered to the substrate heater is ramped up at 1 A/s until the measured temperature reaches around 750 °C. While the two zones are being heated up, a small flow of Ar (200-300 sccm) is delivered through the CVD reaction vessel. The purpose of the argon flow in this step is to purge the CVD vessel of oxygen while temperature reaches 700-800 °C. At these temperatures and in the presence of oxygen, the copper wires and electrodes connected to the Zone 2 heater can oxidize and the connections can potentially fail. At temperatures of 900 °C and higher, silicon can also oxidize, which can lead to cracks in the Zone 2 substrate heater. During this time while the CVD reactor is allowed to thermally stabilize for 5 minutes, the catalyst chips are prepared. Squirting a few drops of Isopropanol onto the catalyst surface and drying them clean with nitrogen removes most dust and organic contaminants.

The following steps outline a warm-start, which is performed between growth runs. Ensuring that  $H_2$ and  $C_2H_4$  flows are off and only Ar is flowing, the rubber stopper protruding from Zone 2 is removed, 1-4 catalyst chips are placed at the centre of the substrate heater, and the stopper is replaced. This step must be performed quickly so as to minimize the amount of  $O_2$  and  $H_2O$  vapour entering the CVD tube. During this step, it is normal to observe the copper slabs, which are electrically connected to the silicon wafer Zone 2 heater, to become oxidized to a green-brown rainbow-like appearance. Next, Ar flow is increased to 1250 sccm. 10 seconds later, H<sub>2</sub> flow is set to 1400 sccm, followed by immediately increasing the current to the substrate heater at a rate of 5 A/s until the temperature reaches 740-750 °C. This annealing step changes the thin iron film into nanometric iron islands or nanoparticles. Annealing has been argued to also help in strengthening the CNT-substrate adhesion post-growth [73]. In the presence of high temperature and absence of oxygen, it is also normal to observe the copper slabs become reduced to their original colour. After annealing for 1 minute, the flow of  $C_2H_4$  is set to 800 sccm and CNT growth immediately occurs, which can be seen as a thin black film. Typically, a forest 500 µm tall can be grown in 15 minutes, while a forest greater than 1 mm tall can be grown in excess of 30 minutes. Maintaining the flow of H<sub>2</sub> during CNT nucleation and growth has been argued to act as a "vapour etching" reducing agent to desorb amorphous carbon fragments from the catalyst surfaces [76]. By doing so, H<sub>2</sub> helps to reduce the gas-phase pyrolysis of the  $C_2H_4$  so crystalline nanotubes can be grown.

When the desired forest height has been achieved,  $H_2$  and  $C_2H_4$  gas flows are stopped. To ensure minimal sooting of amorphous carbon in Zone 2 and over the grown samples, the substrate heater is maintained at its usual temperature for 30 seconds while the flammable gases, including pyrolyzed hydrocarbons, are purged from the CVD tube and sent to the laboratory exhaust. The current to the substrate heater is then reduced at a rate of 5 A/s down to 0 A. Ar flow is decreased to 100-200 sccm and the samples can be extracted from Zone 2, as shown in the right of Figure 8 below.



Figure 8: Photos of (left) CNT forest samples growing in Zone 2, (right) high aspect ratio fully grown CNT forest

### 2.6. Temperature Optimization

Using a custom-designed LabVIEW program developed by my supervised undergraduate summer student, heating of the substrate heater in Zone 2 can be precisely controlled. LabVIEW has the ability to connect with the Zone 2 substrate power supply through IEEE-488 general purpose interface bus (GPIB) and to the infrared thermometer through RS-232 communications. The program was designed to have cold-start and warm-start capabilities, where setpoint temperature, current ramp-up and ramp-down rates, and growth time can all be specified. A screenshot of the program is shown below in Figure 9. The current delivered to the substrate heater is controlled by a 2 second response time negative feedback loop. By using an automated program, the in-house CVD system can move one step further towards growth reproducibility.

A series of temperature sweeps was performed using the LabVIEW program and shown below in Figure 10. The measured voltage, applied current, and calculated electrical power are shown in parts (a), (b), and (c) respectively as functions of the Zone 2 substrate setpoint temperature. The setpoint temperature was varied from 720-780 °C, while gas flow rates and growth times were held constant. Depending on the length (*L*), width (*W*) and resistivity ( $\rho$ ) of the 500 µm thick ( $t_h$ ) silicon heater, the amount of current and therefore power required to achieve a certain substrate temperature can vary, since  $R = \rho L/Wt_h$ . Power was seen to be nearly linear with increasing temperature setpoint. Using the open source ImageJ image analysis software, the heights of the CNT forests were measured and shown in part (d) of the same figure, assuming a 500 µm thick silicon wafer as a reference. As shown in the CNT sidewall photos below in Figure 11, there was a maximum in CNT growth height at 760 °C. At low temperatures, the iron nanoparticles were lacking in sufficient thermal energy to promote carbon diffusion and precipitation. At high temperatures, the iron nanoparticles sintered into larger particles, which was detrimental towards nanotube growth.



Figure 9: Screenshot of LabVIEW CVD program in "Process Run" mode



Figure 10: (a) Voltage, (b) current, (c) power, (d) average CNT height as functions of measured Zone 2 temperature



Figure 11: Photos of CNT sidewalls grown at varying Zone 2 temperatures
# 2.7. Results of CVD-Grown CNTs

The CNT forests were first imaged by scanning electron microscopy (SEM) by my colleagues, Mr. Mike Chang and Mr. Amir Khoshaman. Operating parameters can be found at the footer of the images below in Figure 12. The top two images are zoomed-out views of the sidewall of a CNT forest sample that show the high anisotropic nature of the forest. On the left is a pristine sample, showing the high degree of alignment. On the right is a sample with a cracked edge from mishandling the sample. The bottom two images are close-ups of a CNT forest that show individual bundles of CNTs. On the left is a pristine sample and on the right is a set of bundles that was damaged and ablated by the high temperatures of laser irradiation.



Figure 12: SEM micrographs of MWCNT forest sidewalls showing (top left) high anisotropic nature of CNTs, (top right) cracked sidewall edge, (bottom left) close-up of bundles of CNTs, (bottom right) damage from laser irradiation

The CNT forests were then imaged by transmission electron microscopy (TEM) operating at a 200 keV (using a field-emission gun) with 0.23 nm point to point resolution. These images were taken through a collaboration with Professor Karen Kavanagh's group at Simon Fraser University. The following images were provided by their group. In order to image the CNTs, clumps of CNT forests were manually exfoliated from their silicon substrates and placed in a folding blank copper grid. The images below in Figure 13 were taken using bright field TEM and suggest an average CNT diameter of 6-8 nm with several walls.



Figure 13: Bright field TEM images

# Chapter 3 – Experimentally-Measured Thermoelectric Parameters of the Carbon Nanotube Forest

# 3.1. Introduction

In order to characterize the figure-of-merit of the carbon nanotube forests, information on the Seebeck coefficient, electrical conductivity, and thermal conductivity must be known. The purpose of this chapter is to introduce the basic theory behind how these parameters were experimentally measured for this work. The custom-made apparatuses to measure those parameters are described. This is then followed by an analysis and comparison of the results with literature values.

### 3.2. Theory Behind the Seebeck Coefficient

Since thermoelectric devices consist of two or more different materials, care must be taken when calculating the overall or effective Seebeck coefficient of the device. If we assume that each material (i = 1,2,3,...) has length ( $L_i$ ), cross-sectional area ( $A_i$ ), Seebeck coefficient ( $\alpha_i$ ), electrical conductivity ( $\sigma_i$ ), and thermal conductivity ( $\kappa_i$ ), then these material parameters can be combined to calculate electrical resistance ( $R_i$ ) and thermal resistance ( $r_i$ ), as in Equations (3-1) and (3-2), respectively.

$$R_i = \frac{L_i}{\sigma_i A_i} \tag{3-1}$$

$$r_i = \frac{L_i}{\kappa_i A_i} \tag{3-2}$$

The effective Seebeck coefficient of the thermoelectric device can be approximated in a manner depending on whether the materials are placed electrically in series or in parallel. Equations (3-3) through (3-6) were adapted from [81]. For a device with its elements connected in series, the effective Seebeck coefficient uses a weighted average of the thermal resistance.

$$\alpha_{eff} = \frac{1}{r} \sum_{i} r_i \alpha_i \tag{3-3}$$

$$r = \sum_{i} r_i \tag{3-4}$$

For a device with its elements connected in parallel, the effective Seebeck coefficient uses a weighted average of the electrical conductance.

$$\alpha_{eff} = R \sum_{i} \frac{\alpha_i}{R_i} \tag{3-5}$$

$$\frac{1}{R} = \sum_{i} \frac{1}{R_i} \tag{3-6}$$

Thermoelectric circuits taking advantage of the Seebeck effect obey three basic laws that are as follows. The *Law of Homogenous Materials* states that a circuit of a single homogenous material cannot sustain a thermoelectric current. In other words, two dissimilar materials (e.g. metal A and metal B) are necessary for a net current to exist. As a consequence to this first law, it can be said that if there exists one junction of dissimilar homogenous materials held at  $T_1$  and a different junction held at  $T_2$ , the resulting thermal EMF is independent of temperatures elsewhere in the circuit (e.g.  $T_3$  and  $T_4$ ).

The *Law of Intermediate Materials* states that the sum of the thermal EMFs in a circuit made up of any number of dissimilar materials is zero if the circuit is held at uniform temperature. As a consequence to this second law, a third homogeneous material (e.g. metal C) could be added anywhere in the circuit, but produces no effect on the net thermal EMF if both of its ends are at the same temperature.

The *Law of Successive or Intermediate Temperatures* states that if a pair of dissimilar homogeneous materials produces an EMF of  $E_{12}$  when its junctions are at temperatures  $T_1$  and  $T_2$ , and produces an EMF of  $E_{23}$  when its junctions are at temperatures  $T_2$  and  $T_3$ , then the total EMF generated when the junctions are at  $T_1$  and  $T_3$  will be  $E_{12} + E_{23}$ .

In practice, the absolute Seebeck coefficient of a single material is rarely measured. This is because the electrodes of a voltmeter must probe the material, whereby the temperature gradient across the material will induce a thermoelectric voltage across the voltmeter leads as well. This will lead to an erroneous measurement of the Seebeck coefficient, since the Seebeck coefficient of the voltmeter leads will be included in the measurement.

### 3.3. Experimental Measurement of the Seebeck Coefficient

Of the three parameters necessary to quantify the figure-of-merit, the Seebeck coefficient is the easiest to measure. To measure the Seebeck coefficient, the sample material under test is sandwiched between two contact electrodes. The contact electrodes should ideally be a material with a high thermal conductivity so that all or most of the temperature gradient is along the material under test. Copper electrodes were used for these measurements, although gold electrodes are also commonly used in the literature. One contact (heat source) is slowly heated up, while the other contact (heat sink) is maintained at 300 K, for example. A pair of thermocouples should be in good thermal contact with the hot and cold sample junctions.

While the absolute coefficient of copper is well-documented [82], the absolute coefficient of silicon can vary depending on its resistivity, and in sign whether it is p-type or n-type. The absolute coefficient of CNTs can also vary from sample to sample. The purpose of these measurements was, using copper as a contact electrode, to determine the temperature-dependent Seebeck coefficient of our silicon and MWCNTs. Their values were used as inputs in a simulation model presented in Chapter 5.

In these experiments, CNT forests approximately 700 µm tall were sandwiched between two identical copper pads, as shown below in the left of Figure 14. The photo in the right of Figure 14 is that of a CNT forest sample with identical silicon substrates on top of and underneath the nanotubes. Results from that device are presented in Appendix A.

Electrically-insulative (grounded tip) K-type thermocouples were placed on the heat source and heat sink surfaces. Adjustable needle-probes were electrically connected to the contact electrodes. Heat was applied to the lower copper-CNT or silicon-CNT junction in these photos through direct heating by digital hot plate or by passing current through a ceramic-insulated silicon wafer undergoing Joule heating, as shown below in the left and right of Figure 14, respectively. The top junction was allowed to cool by convection and radiation to ambient conditions. The resulting voltage developed across the two contact pads was measured with a Fluke 187 digital multimeter with 1  $\mu$ V DC resolution. The Seebeck coefficient can be thus quantified as the potential difference divided by the temperature difference. For the remainder of this work, the Seebeck coefficient will be reported as a function of the average temperature of the two junctions.



Figure 14: Measuring Seebeck coefficient in ambient using (left) digital hot plate and (right) insulated silicon wafer heating sources

The measurements performed under high-vacuum required a slightly modified sample holder, as shown below in Figure 15. On the left is a photo of the sample holder resting in the vacuum chamber. On the right is the electrical schematic, whereby the negative voltmeter lead was connected to the bottom (hot) copper electrode and the positive voltmeter lead was connected to the top (cold) copper electrode. When measuring the Seebeck coefficient of CNTs in the longitudinal direction, the bottom electrode was fixed in place and electrically insulated from the aluminum sample holder and the entire vacuum chamber by a thin slab of vacuum-compatible and high-temperature insulative polymer (PEEK, polyether ether ketone, 334-350 °C melting point [83]). A similar connection was employed for the top electrode. However, the distance between the top electrode and the sample could be adjusted by turning the stainless steel screw appropriately. Two K-type thermocouples were fixed in direct contact with the two copper electrodes to measure the hot and cold junction temperatures. In the schematic on the right, the green arrow represents the laser beam path, and the ellipse represents the shape of the focused laser beam incident upon the junction of the bottom silicon and the CNT forest sidewall.



*Figure 15: Measuring thermoelectric voltage in the longitudinal direction under high-vacuum, (left) photo of sample holder and (right) electrical schematic, where the green ellipse represents the shape of the focused laser beam* 

A different sample holder was employed for measuring the thermoelectric voltage in the perpendicular direction, as shown in the left photo and right electrical schematic of Figure 16 below. These measurements were also performed under high-vacuum. Indium tin oxide (ITO) is a popular type of transparent conductive oxide (TCO) thin film. When deposited on glass, one can essentially have transparent electrodes. ITO was used as the hot electrode to allow the visible-light laser beam to travel through it and heat up the CNT-ITO junction. Although not strictly necessary, ITO was also used as the cold electrode to complete a symmetric device. The CNT samples were rested on a slab of Macor®, a high-temperature and vacuum-compatible ceramic insulator. Portions of the test apparatuses were held in place with insulative Kapton® tape to ensure vacuum compatibility and minimal outgassing, compared with regular adhesive tape.





*Figure 16: Measuring thermoelectric voltage in the perpendicular direction under high-vacuum, (left) photo of sample holder and (right) electrical schematic, where the green ellipse represents the shape of the focused laser beam* 

# 3.3.1. Effective Seebeck Coefficient

Room temperature reference values of the Seebeck coefficient, as well as the electrical and thermal conductivities, of copper, silicon, and a MWCNT forest are shown below in Table 3. In the same table below, L is the length (thickness, for this geometry) and A is the cross-sectional area of the material.

Parameter	Copper	Silicon	CNT Forest
$\alpha (\mu V \cdot K^{-1})$	1.83 [82, 84]	300 [84] (p-type)	24 (∥), 11 (⊥) [85]
$\sigma (S \cdot m^{-1})$	5.79x10 <sup>7</sup> [84]	$4.00 \times 10^4 \ (\rho_m = 0.0025 \ \Omega \cdot cm)$	$1.8 \times 10^3$ (  ), 120 ( $\perp$ ) [85]
$\kappa (W \cdot m^{-1} \cdot K^{-1})$	401 [84]	148 [84]	0.5 (∥), 0.06 (⊥) [85]
$L (\mathrm{mm})$	1.5	0.5	0.7
$A (\text{mm}^2)$	6x6 (Cu-Si-Cu)	6x6	6x6
	18x6 (Cu-CNT-Cu)		

Table 3: Room temperature reference material parameters to calculate effective Seebeck coefficients

From Equations (3-3) and (3-4), the effective room temperature Seebeck coefficient can be calculated for two different thermoelectric devices: Cu-Si-Cu and Cu-CNT-Cu, where the three materials within each device were electrically connected in series. In the Cu-Si-Cu device, the thickness of copper was 3 times as large as the thickness of silicon, however the thermal conductivity of copper was also approximately 3 times as large as the thermal conductivity of copper. Therefore, the thermal resistances for copper and silicon were very close to one another, meaning the Seebeck coefficients will be weighted almost evenly. The room temperature effective Seebeck coefficient of a Cu-Si-Cu device was 143.3  $\mu$ V/K if we assume zero electrical and thermal contact resistance losses.

In the Cu-CNT-Cu device, the cross-sectional area and thickness of the two materials were both different, however, the L/A ratios were in the same order of magnitude. From the literature, the thermal conductivity of a MWCNT forest is more than 800 times smaller than that of copper. Therefore, the room temperature effective Seebeck coefficient was thus most heavily weighted by the Seebeck coefficient of the CNT forest and equal to 23.9  $\mu$ V/K. Again, this is if we assume zero resistance losses.

#### 3.3.2. Experimental Results in Ambient

As a function of temperature, the absolute Seebeck coefficient of doped single-crystal silicon is linear and increasing in the 300-500 K range [86]. Similarly, the absolute Seebeck coefficient of MWCNT forests from the literature is linear and increasing in a similar temperature range [87, 88]. In order to verify these trends, each material was sandwiched between copper electrodes. Copper has a well-established temperature-dependent Seebeck coefficient [82], shown below in the left of Figure 17. The O's are the reference values and the solid line is an interpolated linear fit with an  $R^2$  of 0.999. By performing these experiments, we aim to produce temperature-dependent Seebeck coefficient curves for both silicon and our MWCNT forest to use as an input for the simulations presented in Chapter 5. The temperature-dependent thermal conductivity of copper (red X's) and silicon (blue O's) [84] is shown in the right of the same figure. Overlaid power law interpolation curves in solid lines fit the reference data for copper with an  $R^2$  of 0.969 and for silicon with an  $R^2$  of 0.994.



*Figure 17: (left) Temperature dependence of copper absolute Seebeck coefficient [82], (right) temperature dependence of copper (red X's) and silicon (blue O's) thermal conductivity [84]* 

From the analysis of the room temperature effective Seebeck coefficient of the Cu-Si-Cu device, the effective coefficient was nearly evenly weighted between the two materials. The thermal conductivity of silicon falls faster than copper with increasing temperature, so at higher temperatures, the effective coefficient of this device would have a slightly greater weighting on the absolute coefficient of silicon.

The room temperature effective Seebeck coefficient of a Cu-CNT-Cu device was shown to be nearly exactly equal to the absolute coefficient of CNT due to the much lower thermal conductivity of a MWCNT forest (reported between 0.02 - 1 at 300 K [85, 87, 88]). If the thermal conductivity of a forest of MWCNTs is smaller than that of copper and does not change much in the 300-600 K range [87, 88], the Seebeck coefficient of our CNTs should always mirror that of the effective coefficient of the entire device in that temperature range.

Figure 18 and Figure 19 below show the results from experiments performed on a Cu-Si-Cu and Cu-CNT-Cu device, respectively. The left side plots show the raw data of induced voltage difference versus applied temperature difference. The right side plots show the calculated Seebeck coefficient as a function of the average temperature between hot and cold junctions. It can be seen that the magnitude of induced voltage difference increased linearly with an increased temperature gradient applied across the device consistently for both devices. Both devices showed a positive effective Seebeck coefficient, increasing in magnitude with increasing temperature above room temperature.



Figure 18: (left) Cu-Si-Cu potential difference vs. temperature gradient, (right) effective Seebeck coefficient vs. average temperature



Figure 19: (left) Cu-CNT-Cu potential difference vs. temperature gradient, (right) effective Seebeck coefficient vs. average temperature

Using Equations (3-3) and (3-4) again, the absolute Seebeck coefficient of silicon can be extracted from the Cu-Si-Cu device. The temperature-dependent interpolated curves for the absolute Seebeck coefficient of copper, as well as the temperature-dependent interpolated curves for the thermal conductivity of both materials, were incorporated into the equations. As a simplification to these calculations, we are assuming Ohmic contact and perfect thermal contact.

In the top part of Figure 20, the red X's are a collection of all the data points from part (b) of Figure 18. Shown in green  $\Box$ 's is the Seebeck coefficient of copper, which only varies between 1.8 to 2.0  $\mu$ V/K in this small temperature range. From this, the temperature-dependent Seebeck coefficient of our silicon can be calculated and shown in the blue O's, with a value of approximately 280  $\mu$ V/K at room temperature. Because the coefficient was positive, this also confirms that the silicon was p-type. The black line indicates a linear interpolation of the absolute Seebeck coefficient of silicon fitted with an  $R^2$  of 0.889.

Using the same method, the temperature-dependent Seebeck coefficient of CNTs can be calculated and shown in the bottom part of the figure. Once again, the red X's are all the data points from part (b) of Figure 19 and the green  $\Box$ 's are Seebeck coefficient of copper. Since the thermal conductivity of copper (401 W·m<sup>-1</sup>·K<sup>-1</sup> at room temperature) is greater than that of a forest of MWCNTs, the effective Seebeck coefficient is dominated by the CNT coefficient. This effect would be quite pronounced if the thermal conductivity of the forest is in the 0.01 to 10 W·m<sup>-1</sup>·K<sup>-1</sup> range. Only at unrealistically high thermal conductivities of 100 W·m<sup>-1</sup>·K<sup>-1</sup> (purple +'s) and higher would we expect a more even contribution of both materials. Therefore, we can conclude that the Seebeck coefficient of CNTs is almost identical to that of the Cu-CNT-Cu device at approximately 16.5  $\mu$ V/K at room temperature. This is in agreement with the Seebeck coefficient of MWCNT forests measured at room temperature and reported in the literature [85, 87, 89-91] as being anywhere in the 2-40  $\mu$ V/K range. The black line in the bottom figure indicates a linear interpolation of the absolute Seebeck coefficient of the CNT forest fitted with an  $R^2$  of 0.888.



Figure 20: Extracting absolute Seebeck coefficient of (top) silicon (blue O's) and (bottom) CNTs (various  $\Delta$ 's and +'s) assuming varying  $\kappa_{CNT}$ 

### 3.3.3. Experimental Results in Vacuum

It has been reported in the literature that the electronic properties (resistance, Seebeck coefficient, density of states, etc.) of semiconducting single-walled carbon nanotubes in particular are quite sensitive to gas exposure, where they have potential applications in thermoelectric-based gas sensors. Oxygen-saturated SWCNT bundles and thin films have been shown to have a higher electric conductance than oxygendeficient SWCNTs under vacuum since oxygen has good charge transfer to the nanotubes [92]. The Seebeck coefficient of oxygen-doped SWCNTs is positive (p-type material) under ambient atmospheric conditions. However, as a vacuum is allowed to remove more and more physisorbed oxygen, the Seebeck coefficient transitions to a negative value (n-type material) [92]. Scanning tunneling spectroscopy measurements reveal that the local density of states increases upon a CNT's exposure to oxygen (no states are available in a degassed CNT). It has also been suggested that upon exposure to oxygen, there is weak electron transfer from the CNT wall to the adsorbed oxygen, resulting in a negatively charged defect and scattering channel [93, 94]. With elevated temperatures, other studies have shown the slight changes in the Seebeck coefficient to be fully reversible upon the addition and subsequent removal of various gases (hydrogen, helium, nitrogen) into the vacuum chamber [93, 94]. It was understood that the collisions between gas molecules and CNTs generate non-thermal phonons and dynamic defects that lead to slight increases in 4-point probe resistance and decreases in the magnitude of the Seebeck coefficient. However, the Seebeck coefficient of boron-doped SWCNTs in the literature has shown to be unaffected under vacuum conditions, since substituted boron donates holes to the SWCNT and makes the material permanently ptype [95].

Since the CNTs fabricated in this work are multi-walled and therefore always metallic, we do not expect to observe a sign change in Seebeck coefficient upon removal of oxygen under vacuum. However, the purpose of this measurement was to observe if there would be any changes in the Seebeck coefficient of our MWCNTs in a transition from atmospheric conditions, to high-vacuum conditions, and back to atmospheric conditions. Shown below in Figure 21 is the measured absolute Seebeck coefficient of a symmetric Cu-CNT-Cu thermoelectric device (several exfoliated MWCNT forest bundles placed between two copper slabs). The coefficient was calculated as was before using the temperature-dependent Seebeck coefficient and thermal conductivity of copper, while assuming a constant, but low room temperature thermal conductivity of CNTs. Again, since the thermal conductivity of CNTs is much smaller than that of copper, the Seebeck coefficient of CNTs dominates the effective coefficient.

In this device configuration, heat and electricity both conducted in the perpendicular direction with respect to the CNT growth direction. The thermoelectric device was loaded on top of the insulative silicon wafer substrate heater shown previously in the right of Figure 14. Approximately 4 W of electrical power

was applied to the substrate heater. At 0 minutes and at an average temperature of 355 K, the absolute Seebeck coefficient of the CNTs was 12.5  $\mu$ V/K or approximately half of the value reported previously at a similar average temperature (extrapolated 27.2  $\mu$ V/K at 355 K). The decrease can most likely be attributed to the change in electrical conduction direction of the nanotubes (anisotropic Seebeck coefficient). A similar 2-times reduction in the Seebeck coefficient in the perpendicular direction of a CNT forest is reported in the literature [85, 91, 96].

Within the first 20 minutes when the roughing pump was allowed to evacuate the chamber to milliTorr pressures, a 25% decrease in the magnitude of the Seebeck coefficient was observed. Between 20-120 minutes, the turbo pump was allowed to further evacuate the chamber towards  $10^{-5} - 10^{-6}$  Torr. A further 50% decrease in the magnitude of Seebeck coefficient was observed. In this regime, convective heat transfer can hardly take place due to the very small amount of gas molecules in the chamber. The majority of the heat from the substrate heater was conducted towards the thermoelectric device and radiated outwards, whereby a steady-state situation could be attained after some time. At 120 minutes, the turbo pump was allowed to slow down and an increase in the magnitude of the Seebeck coefficient was observed. Finally, at 170 minutes, the roughing pump was turned off and the chamber was vented for 10 minutes. The Seebeck coefficient was seen to increase in magnitude towards the original value at the beginning of the experiment.

In the literature, degassed mats of MWCNTs have shown a negative Seebeck coefficient [97]. Upon exposure to ambient conditions, the mats crossed-over to a positive Seebeck coefficient after several months. When placed under vacuum at elevated temperatures, the mats again showed a negative coefficient after 12 hours. The vacuum-dependence on the Seebeck coefficient of CNTs is quite multi-factorial, i.e. the Seebeck coefficient is dependent on the morphology of the sample (forest or mat or individual tube, single-or multi-walled, etc.), the kinds and levels of defects on the nanotubes that could promote the formation of locally electron-rich or electron-deficient regions for gas adsorption [97], what gasses were adsorbed to the CNTs prior to degassing, the vacuum pressure, degassing time, and temperature, to name a few. We would expect similar changes in the Seebeck coefficient of our MWCNTs. However, for the purposes of simplifying the simulation study in Chapters 5.3-5.4, we will be using the previously measured temperature-dependent, but oxygen-rich (atmospheric conditions) Seebeck coefficient of a MWCNT forest.



Figure 21: Time evolution of absolute Seebeck coefficient of CNTs measured under vacuum, where open circles indicate rough and turbo pump on/off events

# 3.4. Experimental Measurement of Electrical Conductivity

The electrical conductivity is one of the parameters required to quantify the figure-of-merit of a thermoelectric material. Although information on the electrical conductivity was not required for the previous calculations of the Seebeck coefficient, it would be required for a thermoelectric device with materials connected in parallel with one another, as shown in Equations (3-5) and (3-6). The purpose of gathering information on the electrical conductivity here is to first calibrate and validate the test apparatus by measuring the room temperature electrical conductivity of a known standard, i.e. copper. If the measurements are in an acceptable range of accuracy, the room temperature electrical conductivity of a forest of MWCNTs can then be measured and used to calculate the room temperature figure-of-merit. Although the temperature-dependent electrical conductivity of CNTs was not measured, this information was borrowed from the literature [85, 87, 88] and used in the simulations presented in Chapter 5.

When measuring semiconducting materials, the resistance of probe contacts can become comparable to the sample material resistance. While a two-point probe is much easier to implement, the probe contacts providing current must be separated from those measuring voltage. By doing so, the measurement of contact resistance alongside sample resistance can be eliminated. In a linear arrangement of the pins in a four-point probe apparatus, current (*I*) is allowed to flow between the two outer probes, while voltage (*V*) is measured between the two inner probes. Assuming an equidistant interprobe spacing (*s*) and the sample to be measured is of semi-infinite volume, electrical conductivity ( $\sigma$ ) can be measured and calculated by:

$$\sigma = \frac{I}{2\pi s V F} \tag{3-7}$$

, where F is a unitless geometric factor that corrects for probe location near a sample edge, sample thickness, sample diameter, probe placement, and temperature.

Using micro-adjustable needle probes, a four-point probe station was created. Equidistant probe spacing was verified by optical microscopy. Shown below in Figure 22 is a photo of CNT forest under test in the probe station. A Hewlett-Packard 6624A digital power supply provided constant current through the outer two probes, while voltage was measured across the two inner probes by a Fluke 187 voltmeter or a Keithley 2400 SourceMeter.



Figure 22: Photo of experimental four-point probe station

# 3.4.1. Experimental Results in Ambient

The room temperature electrical conductivity ( $\sigma$ ) of copper, silicon substrates, and carbon nanotube forests was measured using the technique and apparatus described above. The temperature of the lab where measurements were performed was measured to be at 22 °C and each material was tested three times. Shown below in Figure 23 and Figure 24 is the voltage measured across the interior two probes while a current was allowed to flow through the exterior two probes in the four-point probe apparatus, performed on a slab of copper (left) and a silicon wafer shard (right). The electrical conductivity of a CNT forest sample was measured in the same manner both in the longitudinal (along the direction of CNT growth) and perpendicular (along the width of the sidewall) directions. In order to probe a CNT forest on its own, a grown CNT forest on its substrate was first measured, then the forest was manually exfoliated from its substrate and measured again.



Figure 23: Measured voltage as a function of input current in a four-point probe setup for (left) copper and (right) silicon



Figure 24: Measured voltage as a function of input current in a four-point probe setup for (left) silicon-CNT and (right) CNT measured longitudinally (solid black line) and perpendicularly (dashed black line)

The interpolated slope of the V-I curves shown above is  $(2\pi s\sigma F)^{-1}$  and electrical conductivity can be extracted, given an s = 0.5 mm probe spacing. The results are shown below in Table 4, where material thicknesses  $(t_h)$  were used to calculate the Haldor Topsøe [98] geometric factors (*F*). Because large plane slabs of copper and silicon were used for these measurements, the use of an infinite plane sample of finite thickness can be assumed. Along the longitudinal direction of the CNT forest, a geometric factor accounting for a probe array parallel to the sample edge was used. Similarly for the perpendicular direction, a geometric factor accounting for a probe array perpendicular to the sample edge was used.

Interpolating for 22 °C, the reference value of the electrical conductivity of copper is  $5.90 \times 10^7$  S/m [84], and a close value of  $6.21 \times 10^7$  S/m was measured experimentally. The electrical resistivity of silicon was measured to be 0.0023  $\Omega$ ·cm, well within the range of resistivities of the wafers as reported by the

manufacturer (0.001-0.005  $\Omega$ ·cm). Because our measured value of the electrical conductivity of copper was just over 5% off from reference, we can safely assume that our test apparatus is sufficiently calibrated.

Between the longitudinal and perpendicular directions of the CNT forest overtop its substrate, there was surprisingly not much difference in conductivity. The reasons for this were unclear, but it is possible that, the silicon, being mostly electrically-isotropic, influences the forest overtop by providing a conduction path through the silicon. With regards to the CNT forest on its own, the longitudinal direction showed a 3.6 times greater conductivity than the perpendicular direction, as expected. The longitudinal conductivity was in a similar order of magnitude as those reported in the literature for MWCNT forests [87, 88, 91]. However, there was as much as a whole order of magnitude greater conductivity in the longitudinal direction compared to the perpendicular direction reported by one study [85]. Nevertheless, these were different nanotubes grown in different conditions, so this result is reasonable.

Material	Interpolated Slope (Ω)	$t_{h}$ (m)	s (m)	F	σ (S/m)
Copper	5.244x10 <sup>-6</sup>	$1.5 \times 10^{-3}$	$0.5 \times 10^{-3}$	0.978	$6.21 \times 10^7$
Silicon	0.01097	$0.5 \times 10^{-3}$	$0.5 \times 10^{-3}$	0.665	$4.36 \times 10^4$
Silicon/CNT	1 204	3.5x10 <sup>-3</sup>	$0.5 \times 10^{-3}$	0.988*0.9876 (averaged)	252.0
Longitudinal	1.294		0.5810		
Silicon/CNT	1 207	3x10 <sup>-3</sup>	$0.5 \times 10^{-3}$	0.9599 (averaged)	274.8
Perpendicular	1.297		0.5810		
CNT Longitudinal	0.9263	3x10 <sup>-3</sup>	$0.5 \times 10^{-3}$	0.988*0.9876 (averaged)	352.2
CNT Perpendicular	3.422	3x10 <sup>-3</sup>	$0.5 \times 10^{-3}$	0.9576 (averaged)	97.1

Table 4: Experimental electrical conductivity measurements of thermoelectric materials

The temperature dependence of the electrical conductivity of all three of the materials was not measured for this work. The temperature dependence of copper's electrical conductivity is well known from reference texts [84], as shown below in part (a) of Figure 25. For silicon, electrical conductivity is a function of the concentration and mobility of electrons and holes, which are all temperature dependent. Assuming p-type silicon doped by boron that has a room temperature resistivity of 0.001-0.005  $\Omega$ ·cm, conductivity was calculated by the method described in [99]. The mobility models by Klaassen [100, 101] were used, which reasonably fit literature experimental data between 100-500 K. The conductivity has been plotted below in part (b) of Figure 25.

From the literature, the electrical conductivity of CNT forests follows a linearly increasing pattern in the 300-600 K temperature range [87], shown below in part (c) of Figure 25. For the purpose of the simulations presented in Chapters 5.2-5.4 the values from that reference were used, assuming a 10 times reduction in conductivity in the perpendicular direction [85].



*Figure 25: Temperature dependence of electrical conductivity of (a) copper [84], (b) silicon at varying room temperature resistivities [100, 101], (c) MWCNT forest [87]* 

# 3.5. Theory Behind the Thermal Conductivity

The temperature dependence of the thermal conductivity of copper and silicon is known from reference texts. The purpose of this section is to give a background on how the thermal conductivity of carbon nanotubes is measured in the literature. Thermal conductivity was not measured for this work. However, using the experimental induced photo-thermoelectric voltage as a function of incident laser power presented in Chapter 4, the CNT thermal conductivity was empirically-fit using a simulation model presented in Chapter 5.

Suppose a sample has a cross-sectional area (*A*) and length (*L*). If a thermal gradient exists across the sample ( $T_1$  and  $T_2$ ), then thermal conductivity is defined as the ratio of the heat flux to the thermal gradient.

$$\kappa = \frac{Q/A}{\Delta T/\Delta L} \tag{3-8}$$

In practice, thermal conductivity can be estimated simply by placing a heat source and thermocouple to one side of a sample, and a heat sink and thermocouple to the other side, if sample dimensions and heat power are known. This however could pose a problem if the thermocouple probe has dimensions on a similar order as a CNT forest, for example. Heat applied to the sample will be drawn away by the thermocouple and interfere with measurements. The Quantum Design physical property measurement system (PPMS) is able to measure the thermal conductivity of CNT forests using this method and alleviates the aforementioned problem by using highly-accurate micro-thermocouples. Samples are attached to disk-shaped gold-plated copper electrodes using silver epoxy [85].

Other methods to measure the thermal conductivity of CNTs have been reported in the literature. One method uses the laser from a Raman spectroscope to focus a spot of known power to locally heat the CNTs [102]. By comparing the Stokes and Anti-Stokes Raman spectra intensities, the temperature and thus the thermal conductivity of the nanotubes can be measured.

A more common, but elaborate, method involves the measurements of density ( $\rho_d$ ), specific heat capacity at constant pressure ( $c_p$ ) and thermal diffusivity (*D*) [14, 16, 88, 96, 103-105]. To measure the density of bulk CNTs in the literature, it is common to hot press powders of CNTs into a dry pellet. Density is first measured by Archimedes's method, which requires measurements of the dry sample weight, suspended weight, saturated weight, and density of the saturating/suspending liquid to calculate the bulk density of the pellet [106]. Heat capacity is then measured by differential scanning calorimetry (DSC), whereby a sample pan containing a known weight of CNTs and an empty reference pan are both heated at the same rate. The amount of heat needed to increase the temperature of the sample pan and the reference pan are measured as a function of temperature and the heat capacity is calculated as the amount of heat supplied divided by the temperature increase. Lastly, thermal diffusivity is measured by a laser flash apparatus (LFA), whereby a short laser pulse irradiates one side of a plane-parallel CNT sample. Heat is allowed to diffuse through the sample and reach an infrared detector on the other side. This is measured as a function of time to reach half maximum intensity. Thermal diffusivity shown below in Equation (3-9) is a function of the sample thickness ( $t_h$ ) and the time ( $t_{t_2}$ ). These measured parameters can be used directly to calculate thermal conductivity, as shown in Equation (3-10).

$$D = 0.1388 \cdot \frac{t_h^2}{t_{1/2}} \tag{3-9}$$

$$\kappa = D\rho_d c_p \tag{3-10}$$

A literature survey was conducted to compare experimental results of measured thermal conductivities using a few techniques. As seen below in Table 5, there is no observable trend in  $\kappa$  as a function of CNT height or measurement temperature. Thermal conductivity varies as much as three orders of magnitude and the reasons behind this are not well explained or understood. We can assume that each measurement is

performed on different nanotubes with varying chiralities, lengths, temperatures, purities, or defect levels, all of which can affect thermal conductivity. As well, the different measurement techniques can cause discrepancies if the equipment is not calibrated.

Sample	Measurement	к	T (K)	<b>CNT Height</b>	Ref.
	Technique	(W•m <sup>-1</sup> •K <sup>-1</sup> )			
MWWCNT forest (CVD)	LFA, hot disc	0.035-0.05 (atm)	300-500	2 mm	[87]
		0.02-0.025 (vac)			
MWCNT forest (CVD)	LFA	3-6.4 (  )	300	> 2 mm	[107]
		0.08-0.14 (⊥)			
SWCNT and MWCNT	LFA	8.3	300	200 µm	[108]
film mixture (CVD)					
MWCNT film (PECVD)	LFA	12-17	300	10-50 µm	[109]
MWCNT forest (PECVD)	LFA	450-1200	218-473	20 µm	[110]
MWWCNT forest (CVD)	Quantum Design PPMS	Increases linearly	2-300	1.5 mm	[89]
		to 2.5 at 300 K			
MWCNT forest (water-	Quantum Design PPMS	0.002-1 (  )	1.8-390	2.5-5.9 mm	[85]
assisted CVD)		0.006-0.06 (1)	50-300		
Spark plasma sintered	Archimedes' method,	0-32 (  )	10-320	2-3 mm	[91]
MWCNT forest (CVD)	Quantum Design PPMS	0-19 (⊥)			
DWCNT bundles purified	DC T-type method	25-40	240-340	8.3 mm	[24]
from CVD film					
MWCNT forest (CVD)	Phase sensitive	250		1-100 μm	[111]
	transient thermo-				
	reflectance				

Table 5: Literature survey of experimental thermal conductivity of aligned MWCNTs

The thermal conductivity of carbon nanotubes can also be studied theoretically by classical molecular dynamics simulations. Classical molecular dynamics solves Newton's equations of motion for a given set of atoms that interact with each other through empirical interatomic potentials (e.g. Tersoff, Brenner, reactive empirical bond order (REBO), and adaptive intermolecular REBO (AIREBO)). However, electrons are not explicitly modelled using this technique, so electron-electron and electron-phonon interactions cannot be studied explicitly. Because the  $\kappa_{ph}$  of both SWCNTs and MWCNTs is dominant over  $\kappa_{el}$  at all temperatures, it is often safe to neglect the electronic portion of thermal conductivity when simulating this material [112, 113].

As mentioned previously in Chapter 1.6, the thermal conductivity of SWCNTs fit to experimental data in the literature was seen to follow a  $1/(\alpha T + \beta T^2)$  dependence due to Umklapp phonon-phonon scattering and second-order three-phonon scattering [36]. Thermal conductivity was also seen to be a function of nanotube length (*L*) in µm, shown as a modified version of [36] as:

$$\kappa(L,T) = \left[\alpha T + \beta T^2 + \gamma \left(1 + \frac{l_{0,ph}}{L}\right)T^{-2}\right]^{-1}$$
(3-11)

, where  $\alpha = 3.7 \times 10^{-7} \text{ W}^{-1} \cdot \text{m}$ ,  $\beta = 9.7 \times 10^{-10} \text{ W}^{-1} \cdot \text{m} \cdot \text{K}^{-1}$ , and  $\gamma = 9.3 \text{ W}^{-1} \cdot \text{m} \cdot \text{K}^{3}$  are fitting parameters and  $l_{0,\text{ph}} = 0.5 \text{ }\mu\text{m}$  is the room temperature phonon mean free path. From this expression, the dependence on CNT height vanishes with higher temperatures as thermal conductivity is no longer limited by phonons scattering with the sample boundaries, but only through phonon-phonon scattering. Although there are many reports of the simulated thermal conductivity of SWCNTs, to our knowledge, there are no reports on the studies of MWCNTs. Perhaps this is due to the complexity of the system when many more atoms are needed to simulate a MWCNT. Nevertheless, there certainly do not seem to exist any high temperature (e.g. T > 600 K) experimental or theoretical studies on forests of MWCNTs.

### 3.6. Summary

The absolute Seebeck coefficients of silicon and CNTs have been measured using the apparatuses described previously. The dependence on temperature has been extracted, given known electrical and thermal properties of the copper contact electrodes. The coefficient of CNTs agrees well with the literature values. The room temperature electrical conductivity of all materials used in the thermoelectric devices was measured. The results for the conductivity for silicon and copper were both in very good agreement with their reference values. The room temperature electrical conductivity of the CNT forest exhibited an enhancement in the longitudinal direction, similar to what is reported in the literature. The thermal conductivity of silicon and copper is known from references. However, it was not experimentally measured for CNTs in this work. Instead, a temperature-dependent model was empirically-fit and discussed in Chapter 5.

# Chapter 4 – A "Heat Trap" Thermoelectric Energy Converter Using Carbon Nanotube Arrays

# 4.1. Introduction

To better understand the "Heat Trap" effect in a forest of carbon nanotubes and whether it can be utilized in thermoelectric energy generation, different experiments were carried out under vacuum. Samples were placed in vacuum near a viewport to allow one to focus a visible laser onto the nanotube forest sidewall. Two device configurations were investigated. One involved conduction along the nanotubes and the other involved conduction perpendicular to the nanotubes.

# 4.2. "Heat Trap" – Localized Laser Heating Under Vacuum

Devices consisting of vertically-aligned carbon nanotube forests sandwiched between two electrodes were loaded into a vacuum chamber using the custom-machined sample holder described previously in Chapter 3.3. The vacuum chamber was pumped down to 10<sup>-6</sup> Torr with an 80 L/s turbopump and to low in the 10<sup>-7</sup> Torr range with a 300 L/s turbopump. The chamber pressure was measured with an MKS cold cathode pressure gauge. Rather than directly heating by a hotplate or resistive silicon wafer, the "Heat Trap" effect [30] was utilized, which consists of localized heating of a CNT forest by focused light. The laser used in the following experiments was an optically-pumped, single-mode, and continuous-wave semiconductor laser, namely the Coherent Verdi V5 (532 nm). The schematic shown below in Figure 26 is a top-down view of the experimental setup. Due to the position of the laser on the optical table, several mirrors were installed to steer the beam towards the vacuum chamber, through the viewport, and at the thermoelectric device-under-test.



Figure 26: Top view schematic of photo-thermoelectric experimental apparatus

Average laser power was first measured with a Newport optical power meter. The left of Figure 27 below shows the measured optical power as a function of the setpoint power that the user sets at the laser control panel. Linearly-interpolating for this curve, there was consistently 73.2% power transmission, meaning that nearly 27% of the light leaving the laser was lost due to absorption or stray reflections by the mirrors and lens. This was confirmed by measuring the optical power before and after the various optical components. Considering that the final viewport window was made of BK 7 borosilicate glass with 92.3% transmission at 532 nm [114], the two transmission coefficients can be multiplied together. Therefore, 67.5% of the setpoint power is what enters the UHV chamber and irradiates the device-under-test. The photo on the right of the same figure shows the 1"x1" plano-convex cylindrical lens mounted on an optical holder (foreground). The green light from the laser was focused through this lens, which then passed through the BK 7 viewport window (background), and onto the thermoelectric device-under-test.





Figure 27: (left) Measured laser power as a function of laser setpoint power, (right) photo of mounted plano-convex cylindrical lens focusing laser through vacuum chamber viewport and onto thermoelectric device-under-test

The purpose of using the plano-convex cylindrical lens (f = 150 mm) was to heat the lower junction between the silicon slab and the sidewall of the CNT forest uniformly, or as uniformly as possible. Since a plano-convex cylindrical lens focuses incoming light only in one direction, the radius of the laser spot size in the *x*-direction ( $r_x$ ) is actually equal to the original beam radius,  $r_0 = 1.125$  mm [115]. The half-divergence angle of the laser beam can be calculated as [116]:

$$\theta_{1/2} = \frac{2M^2\lambda}{\pi(2r_0)} \tag{4-1}$$

, where  $M^2$  is a spatial characteristic for the laser beam quality and  $\lambda$  is the wavelength (532 nm). From this equation, the half-divergence angle is 0.15 mrad, assuming  $M^2 = 1$  for the perfect TEM<sub>00</sub> lowest order laser mode. Since the laser manufacturer reports a half-angle of less than 0.25 mrad [115], the upper limit of the reported angle can be used (rather than the calculated value) for a more conservative approximation. The

radius of the laser spot size in the y-direction ( $r_y$ ), focused with a lens of focal length f = 150 mm, is simply equal to  $f \cdot \theta_{\frac{1}{2}}$  [116] or 37.5 µm. This focused line width was sufficient to heat the silicon-CNT junction on each "chip." However, to observe "Heat Trap" conditions, at least an order of magnitude more optical power was required due to the unfocused spot shape in the *x*-direction, compared with a traditional circular lens that focuses light in both directions to an overall smaller spot size (higher heat intensity).

### 4.3. Longitudinal Conduction

In the first experiment, incident light from the laser source was directed towards the lower junction of a silicon-CNT-silicon sandwiched configuration, as schematically shown below in Figure 28. Copper contact electrodes placed above and below the device served as the probes to measure the induced voltage in the longitudinal direction. Vacuum-compatible wires wrapped with insulative Kapton® tape were electrically connected from each copper electrode to the electrical feedthrough for voltage measurements outside the vacuum chamber. In the same schematic, temperatures can be assigned to each face or junction.



Figure 28: Experimental schematic for longitudinal conduction with symmetric copper electrodes, where the green ellipse represents the shape of the focused laser beam

Shown below in Figure 29 is a plot of the induced voltage as a function of time upon heating at varied laser powers. For all upcoming discussion and plots, the laser power referred to is the actual amount of laser power incident upon the thermoelectric device, taking into account the net transmission coefficient. An incandescent glow was visually seen on the CNT sidewall beyond 67.5 mW, which confirmed that "Heat Trap" conditions were met at this threshold.

Under no laser heating, there was no temperature difference across the device, so there was no induced potential difference, as expected. As soon as the laser was allowed to illuminate the lower silicon/CNT junction, there was a rapid drop to a negative value, followed by a slow and gradual decrease in magnitude of the voltage. The magnitude of the negative peak increased consistently with increasing laser power. From the measurements of the Seebeck coefficients presented in Chapter 3.3.2, the absolute Seebeck coefficients were positive for all three materials, meaning the electromotive force should drive the current through the materials from the hot to the cold junction. In other words, current should travel from the hot lower junction,

through the CNTs longitudinally, and towards the cold upper junction. There should be a positive voltage formed across the junction in this thermoelectric device schematic. The negative voltage plotted below showed the opposite trend, as if the upper junction was "hotter" than the lower junction. However, this is fundamentally not possible. The laser was aimed at the lower junction, so the lower electrode should always be hotter and therefore a positive voltage should always be induced. Below, we will show that this expectation is based on an oversimplified view of the device and, in fact, the situation is more complex.



Figure 29: Sample 1 – Induced voltage as a function of time for varying incident laser powers with symmetric copper electrodes

In order to better understand the temporal effects of this device, the overall thermoelectric circuit can be broken down into its components. We assume that all contacts between materials were Ohmic contact:

$$V_{net} = V_{Cu,bottom} + V_{Si,bottom} + V_{CNT} + V_{Si,top} + V_{Cu,top}$$
(4-2)

$$V_{net} = \int_{T_2}^{T_1} \alpha_{Cu,bottom} dT + \int_{T_3}^{T_2} \alpha_{Si,bottom} dT + \int_{T_4}^{T_3} \alpha_{CNT} dT + \int_{T_5}^{T_4} \alpha_{Si,top} dT + \int_{T_6}^{T_5} \alpha_{Cu,top} dT$$
(4-3)

$$V_{net} = \alpha_{Cu}(T_1 - T_2) + \alpha_{Si}(T_2 - T_3) + \alpha_{CNT}(T_3 - T_4) + \alpha_{Si}(T_4 - T_5) + \alpha_{Cu}(T_5 - T_6)$$
(4-4)

, where  $T_1$  through  $T_6$  have been previously schematically shown in Figure 28. Since the Seebeck coefficients of all three materials were positive, the sign of  $V_{net}$  is ultimately determined by the temperature gradients across each material. Naturally,  $T_3$  should be the largest since that is the junction upon which the laser is centred.  $T_3$  should be larger than  $T_2$ , which should be larger than  $T_1$ . Since the Seebeck coefficient of copper is much smaller than that of silicon in this configuration, the voltage across the bottom silicon should be negative, and the voltage across the bottom copper should be less negative. In the other direction of the device, the temperatures at each junction or face should follow a similar behaviour, which should be  $T_3 > T_4 > T_5 > T_6$ . If we at first assume that the thermal conductivity of the CNT forest is small, the temperature gradient across the forest should be large, and the induced voltage should be large and positive.

The voltages across the top silicon and copper electrodes should also be positive, but much smaller as a result of a much smaller temperature gradient.

Given this information, we now focus our attention to the temperature gradients across the lower 3 materials, since the temperature gradient across the top 2 materials can be assumed to be negligible in comparison. Immediately after the laser is allowed to heat the lower Si-CNT junction, we would initially expect an abruptly large temperature gradient across both lower copper and silicon electrodes, which would result in similarly abrupt negative voltages. Because of their fairly high thermal conductivity (> 100 W·m<sup>-1</sup>·K<sup>-1</sup> at 300 K for both materials, from Figure 17 in Chapter 3.3.2), we would predict that the temperature difference across these materials would decrease (fairly slowly) and their induced negative thermoelectric voltages would diminish towards zero as well.

As a toy example, let's consider a small slab of copper ( $6x6x1.5 \text{ mm}^3$ ) sitting at  $T_i = 300 \text{ K}$  and heated from a source that is set at  $T_H = 500 \text{ K}$ . The following equations can be used to estimate how long this body would take to be uniformly heated to 500 K:

$$hA(T_H - T)dt = mc_p dT \tag{4-5}$$

$$e^{\frac{-hA}{\rho_d V c_p} t} = e^{\frac{-\kappa t_h}{\rho_d V c_p} t} = \frac{T(t) - T_H}{T_i - T_H}$$
(4-6)

, where *h* is the heat transfer coefficient,  $\kappa$  is the thermal conductivity, *m* is the mass,  $c_p$  is the specific heat capacity at constant pressure,  $\rho_d$  is the volumetric mass density,  $t_h$  is the thickness, *A* is the cross-sectional area, and *V* is the volume. Material parameters for copper are presented later on in Table 7 in Chapter 5. Assuming no heat is lost by the copper slab, it would take around 3 seconds for the copper slab to reach 500 K. However in reality, this would take much longer due to the heat transfer from copper to its surrounding materials and radiation into the vacuum chamber.

At the same time and immediately after the laser irradiates the lower portion of the CNT forest, we would also initially expect a sudden large temperature gradient across the CNT forest longitudinally. This would in turn induce a sudden large positive voltage. However, since the Seebeck coefficient of silicon has been previously shown to be much larger than the Seebeck coefficient of a MWCNT forest, the induced negative voltage from silicon would initially outweigh the positive voltage from the CNTs.

Over time and upon low incident laser powers, where there is no "Heat Trap" effect, the thermal conductivity of the CNT remains relatively high over time. Although high, the thermal conductivity is still lower than that of copper and silicon. During this time, the temperature gradient across all materials should be decreasing, where the gradient across copper and silicon would decrease faster than that across the CNTs.

Therefore, we would expect the negative contributions from the copper and silicon to reduce in magnitude more quickly than the positive contributions from the CNT forest. As a function of time, the net induced voltage across the entire device should start off at 0, jump to negative values, and then decrease in magnitude towards less negative values or even zero.

Upon higher incident laser power (above 67.5 mW of power), the "Heat Trap" effect happens very fast whereby the thermal conductivity of CNTs drops quickly. Therefore, the temperature gradient across CNTs should be very high and fairly constant time. This would translate to a positive and relatively constant contribution to the net induced voltage across the entire device. Discussed earlier, the temperature gradients across the copper and silicon should decrease with time as the materials eventually reach a thermal equilibrium. Those two materials would contribute a negative and decreasing in magnitude contribution to the net induced voltage. At some point, the positive voltage contributions from the CNT forest could overtake the two negative and decreasing contributions from both lower copper and silicon electrodes, and we could observe a crossover to positive voltages.

To test this theory again, a different CNT device was loaded into the same test apparatus. The power sweep was repeated with one additional higher power (607.5 mW). The laser was left to irradiate the lower junction, but for a much longer period of time, as shown below in Figure 30. With the second device, we observed a nearly identical behaviour to the first device within the first 10 minutes (which was the duration of the experiment for the first device), as shown in the left. As shown in the full time-scale plot in the right, we observed a crossover to positive voltages at only the higher laser powers (202.5-607.5 mW), which was sustained over time. The characteristic incandescent glow of the hot spot on the sidewall of the CNT forest was also clearly observed at these laser powers.

We believe that beyond a threshold of 67.5 mW, we were operating under true "Heat Trap" conditions, where due to a sudden drop in thermal conductivity of the CNT forest (in all directions), we maintained a localized heat spot at the lower silicon-CNT junction. This created a large temperature gradient across the nanotube forest that induced a positive voltage larger than the two negative voltage contributions from the two lower electrodes. The induced voltage reached a steady state in excess of 30 minutes, when we believe the thermal conductivity and the temperature gradients of all materials had reached a thermal equilibrium. However, the open-circuit voltage at 607.5 mW of laser power was lower than expected. We believe that at such large laser powers, the CNT forest was likely damaged by irradiation, causing irreversible decreases in thermoelectric output. At the lower powers, we believe that the positive voltage from the CNT forest nearly balanced the negative contributions from the lower electrodes. This might explain why we observed a decay to close to 0 mV  $\pm$  10  $\mu$ V at steady-state. A more in-depth simulation of the temporal behaviour based on thermal effects will be presented in Chapter 5.3.4.



Figure 30: Sample 2 – Induced voltage as a function of time for varying incident laser powers with symmetric copper electrodes plotted on a (left) reduced time scale and (right) full time scale

Since this is a thermoelectric device that converts a temperature difference into an induced potential difference, we could also suggest that there are some electrical temporal effects at play as well. In a way, this exponential fall and rise was reminiscent of electrically discharging and charging a capacitor. The voltage curves from before can be fitted by exponential functions, as shown in Equation (4-7) for discharging and Equation (4-8) for charging. Table 6 below summarizes the fitting parameters used, where  $dV_{0,d}$  and  $dV_{0,c}$  are the (mV) voltage offsets for discharging and charging, respectively, d and c are the exponential multipliers,  $\tau_d$  and  $\tau_c$  are the electrical RC time constants, and  $t^*$  is the turning point time in seconds.

Common to both equations, the vertical offset and exponential multiplier coefficients in general increased to larger magnitudes with greater incident laser powers. The RC time constants for discharging increased in magnitude with increasing laser power, then abruptly decreased at 607.5 mW. We attributed this to the likely damage occurring at this very high power. The RC time constant for charging was more than an order of magnitude larger and showed the opposite trend. There was a decrease in magnitude with increasing incident power, followed by an abrupt increase at 607.5 mW. At first glance, it is not clear why the time constants were larger for charging. Perhaps the internal resistance of the device increased as a consequence of the device reaching a thermal equilibrium. There was however no obvious trend in the cross-over time, which was around 2 minutes for all laser powers. The overlaid exponentially-fitted curves are plotted in Figure 31 below.

$$\Delta V = V_{0,d} + d \cdot (e^{-t/\tau_d}), (0 < t \le t^*)$$
(4-7)

$$\Delta V = V_{0,c} + c \cdot \left(1 - e^{-t/\tau_c}\right), (t^* < t < \infty)$$
(4-8)

Laser Power (mW)	$V_{\theta,d}\left(\mathbf{mv}\right)$	<i>d</i> (mv)	$\tau_d$ (sec)	$V_{\theta,c}$ (mv)	<i>c</i> (mv)	$\tau_c$ (sec)	<i>t</i> * (sec)
6.75	-0.00920	0.01527	18.35	-0.01393	0.01983	721.5	120
20.25	-0.03811	0.04722	18.59	-0.05352	0.05242	615.1	140
33.75	-0.07148	0.07030	18.76	-0.0949	0.08709	612.5	105
67.5	-0.1238	0.1152	20.57	-0.1726	0.1728	587.4	125
202.5	-0.3585	0.3618	21.06	-0.5100	0.5083	523.6	130
337.5	-0.5542	0.5716	22.72	-0.8264	0.8538	481.6	135
472.5	-0.6508	0.6708	25.72	-1.002	1.178	480.0	135
607.5	-0.8367	0.6043	11.10	-1.151	1.266	675.5	105

Table 6: Exponential fitting parameters used to determine RC time constants



Figure 31: Sample 2 – Induced voltage as a function of time for varying incident laser powers with symmetric copper electrodes, with fitted exponential functions overlaid (black)

Including all wiring from the thermoelectric device to the measurement tools, the internal resistance was on the order of 1.5 k $\Omega$ . Using the RC time constants above, we can estimate the capacitance of the device to be on the order of tens of milliFarads for discharging and hundreds of milliFarads of charging. Reported in literature, forests of MWCNTs have been shown to be promising candidates for supercapacitor electrodes, where specific capacitances can be in the 27-365 F/g range [117-119]. In order to estimate the mass of the CNT forest, we have to make an assumption on its packing or array density. For this calculation, we are assuming our CNT forest to have a 10% density [69, 111] in each of the directions perpendicular to the growth direction (i.e. 1% carbon forest density or 22.6 kg·m<sup>-3</sup>). As a quick comparison, MWCNT forests in literature have been reported to have a 60 kg·m<sup>-3</sup> array density [85], or in other words, 2.7% carbon density. Using reference values for the specific capacitance, our forest should be on the order of 15-207 mF, assuming a bulk volume of 6x6x0.7 mm<sup>3</sup>. This agrees very well with the estimate of the capacitance from the experimentally-fitted RC time constants.

### 4.4. Perpendicular Conduction

Since we know that the thermal conductivity of carbon nanotube forests in the perpendicular directions can be 1-2 orders of magnitude smaller than that in the longitudinal direction, as previously shown in Table 5, and that thermoelectric device efficiency is enhanced when thermal conductivity is reduced, a new thermoelectric device was fabricated to attempt to take advantage of this intrinsic and anisotropic material property. In the dimensionless figure-of-merit, shown previously in Equation (1-6), the square of the Seebeck coefficient, the electrical conductivity, and the absolute temperature are in the numerator, while thermal conductivity is the denominator. From the literature, the room temperature Seebeck coefficient of a MWCNT forest in the perpendicular directions is half of that in the longitudinal direction [85]. From the same report, the room temperature electrical conductivity is one order of magnitude smaller in the perpendicular direction. Therefore, if the perpendicular thermal conductivity of CNTs is more than 40 times smaller than the thermal conductivity in the longitudinal direction, *ZT* and the overall energy generation efficiency will be enhanced.

To ensure sufficient electrical contact with the nanotube forest sidewalls and to still allow the laser beam to heat one junction, indium tin oxide (ITO) transparent electrodes with 84% visible light transmission at 532 nm [120] were used. In the perpendicular direction, the hot junction is therefore the region between one ITO electrode in contact with one of the four CNT sidewalls, and the cold junction is the region between another ITO electrode in contact with the CNT sidewall on the opposite face of the forest. Shown below in Figure 32 are the device schematics.

From before, 73.2% of the power that the user sets at the laser control panel after reflecting off all the mirrors and through the plano-convex cylindrical lens was measured. If we know that the BK 7 viewport has 92.3% transmission and that ITO has 84% transmission at 532 nm, the net transmission coefficient is calculated to be 56.7%. For all upcoming discussion and plots, the laser power referred to is the actual amount of laser power incident upon the thermoelectric device, taking into account the net transmission coefficient here.

An ideal perpendicular conduction device would be simply ITO-CNT-ITO. However, it is in practice difficult to exfoliate a CNT forest from its substrate while maintaining its 3D shape. The original silicon substrates are required for support. Initially, each ITO electrode was in contact with both the silicon and CNT sidewall as shown in the left. In this configuration, CNTs were connected to the silicon substrate electrically and thermally in parallel. However, it should be noted that when the silicon "chips" are diced by a diamond scribe, the cleaved edge is not a clean cut, but rather a macroscopically rough edge. The thin film catalyst located at the edges of the cleaved silicon chip can potentially be damaged in the process. Therefore, when CNTs are grown vertically upwards by CVD, the CNT forest is not truly grown right on

the edges. In this configuration, we cannot be certain that we were making sufficient contact with CNTs, but we do contact the silicon since it is a rigid boundary.

In the second configuration (shown on the right side of the figure), the ITO electrodes were lifted by 500  $\mu$ m (thickness of silicon), rested on the silicon substrate, and brought towards one another. In this configuration, the ITO electrodes compressed CNT forest sidewalls inwards and we can be fully certain we were making electrical and thermal contact with the CNTs.



Figure 32: Experimental schematic for perpendicular conduction with symmetric ITO electrodes in contact with (left) silicon-CNT junction and (right) with only the compressed CNT sidewall, where the green ellipse represents the shape of the focused laser beam

A set of laser power sweeps up to 115 mW was conducted on the same CNT sample before and after the compression for the second configuration. Part (a) of Figure 33 below shows the laser sweeps for electrical contact with both the silicon and CNT sidewall and part (c) shows the same laser sweeps for electrical contact only with the compressed CNT sidewall. Rather than having a very slow temporal response, the thermoelectric device constructed with symmetric ITO electrodes stabilized at an open-circuit voltage value within 5 seconds. To confirm the steady-state value, each laser power was allowed to heat the sample and stabilize for 2 minutes. Between the two, the second electrode configuration showed more than doubling of the output voltage at the same laser powers. This was most likely due to better electrical and thermal contact with the CNT forest and an overall lower internal resistance of the device.

Decreasing the power in the same increments and time intervals showed slight hysteresis, as shown in parts (b) and (d) of Figure 33 below for the two configurations. Interestingly, the voltage hysteresis was towards smaller values when cooling in the first configuration, while it was towards larger values when cooling in the second configuration. Since silicon has a larger thermal conductivity than carbon nanotubes (especially compared to that in the perpendicular direction), this suggests that when ITO was in contact with both silicon and CNTs and the laser was reduced in power, heat was drawn away into the silicon thermal pathway more rapidly than into the CNT pathway alone.



Figure 33: (left) Steady-state induced voltage and (right) hysteresis of induced voltage as functions of incident laser power for (top) ITO-Si/CNT-ITO and (bottom) ITO-CNT-ITO devices

In order to quantify the output electrical power of this thermoelectric device, the open-circuit voltage, current flow, and internal resistance were all measured at each step in the laser power sweep and shown in parts (a), (b), and (c) of Figure 34 below respectively. These measurements were performed only on the latter electrode configuration where ITO was in contact with only the CNT sidewalls. As expected, voltage increased steadily with more laser power and current flow in the  $\mu$ A range was seen to increase in nearly an identical shape. At around 60 mW of laser power, there was a slight jump in voltage and current.

Under ambient pressure, the internal resistance of the device was 245  $\Omega$ , which steadily dropped to 198  $\Omega$  at rough milliTorr pressure. After the crossover to the turbo-pump, the resistance further dropped to 181  $\Omega$  at 5x10<sup>-5</sup> Tor and ultimately settled at around 139  $\Omega$  at 1.3x10<sup>-6</sup> Torr. As the vacuum chamber was pumped down, more and oxygen molecules were desorbed from the surface of CNTs and this potentially had an effect of decreasing the internal resistance of the thermoelectric device. We observed a slight decrease in internal resistance between experiments 1 through 3 performed in chronological order while the vacuum was further pumped down.

A similar observation was reported on the study of SWCNT mats, where the four-probe resistance of the mat decreased with increasing pumping time [93]. The resistance of the mat would first increase by 2-10% with the addition of oxygen, nitrogen, or helium, followed by a decrease with the removal of those species. It was understood that these increases in resistance were due to an increased scattering rate from the dynamic defect states of the temporarily adsorbed gases, or due to the generation of collisions between the gases and the CNT walls causing localized phonons. Although oxygen is a dopant and reduces the resistance of a CNT (the opposing effect), this suggests that the dynamic scattering effects dominate the effects of doping.

Output power shown in part (d) can finally be calculated given all the electrical parameters. Electrical power in the tens of nanoWatts range was seen to increase with increasing laser power. Power conversion efficiency as a function of laser power was seen to be in the low  $10^{-5}$  %, as shown below in Figure 35, and increasing with increasing laser power. While the efficiency of a photovoltaic cell is determined by its external quantum efficiency, which remains relatively constant and falls off above a certain temperature, the fact that power conversion efficiency increased with increasing laser power here helps prove that this is the thermoelectric effect, rather than the photovoltaic effect. At higher temperatures, the exponential Boltzmann tail is enlarged and there is a higher probability for electrons to surmount the potential energy barrier and travel from the material in which they have lower energy and into the material in which they have higher energy. As well, the thermal conductivity of CNTs falls off with increasing temperature (from higher incident laser powers), resulting in a higher temperature gradient, a higher induced voltage, and a higher power conversion efficiency.



*Figure 34: (a) Output voltage, (b) output current, (c) internal resistance, (d) output electrical power of an ITO-CNT-ITO thermoelectric device as functions of incident laser power* 



Figure 35: Power conversion efficiency as a function of incident laser power, assuming 56.7% optical transmission

# 4.5. Summary

In this chapter, we have shown in two proof-of-concept devices that both longitudinal and perpendicular conduction was feasible, whereby the sidewall of a CNT forest was irradiated by a 532 nm laser. In the case of longitudinal conduction, high laser powers were required to induce "Heat Trap" conditions and sustain an open-circuit voltage. Below a threshold incident laser power of 67.5 mW, the temperature gradient across the silicon was believed to be similar to that across the CNT forests, so a very low net voltage could be induced. Beyond the threshold power, the thermal conductivity of CNTs fell with increasing temperature, thus promoting a net positive voltage. In the case of perpendicular conduction, much lower laser powers were needed to sustain a similar temperature gradient, owing to the anisotropic thermal conductivity of CNTs. As much as  $2x10^{-5}$  % device efficiency was achieved at the highest incident laser power.

# Chapter 5 – Simulation Study

### 5.1. Introduction

In order to study the thermoelectric effect using simulations, we chose finite-element analysis using COMSOL Multiphysics [121], where the relevant physics modules must be incorporated. The **Heat Transfer in Solids** physics within the **Heat Transfer** module solves Fourier's Law in a conservation of heat energy (heat in = heat out) to study the temperature of a body, given the volumetric mass density, heat capacity, and thermal conductivity [122]. The **Electric Currents** physics within the **AC/DC** module uses the electric potential as a dependent variable to study the electric field, potential, and current distributions of a body [123]. Together, these can be coupled in a "multiphysics" scheme to study the Seebeck and Peltier thermoelectric effects, where temperature (*T*) is the coupling variable.

### 5.1.1. Heat Transfer Module Definitions

Heat transfer is the study of the flow of energy due to a temperature difference and is characterized by three mechanisms. Heat transfer by *conduction* involves the transfer of the internal energy of particles (molecules, electrons, atoms, phonons, etc.) by diffusion and collisions within a body due to a temperature gradient. Heat flux is due to thermal conduction and is proportional to the temperature gradient, but opposite to it in sign. It is described by Fourier's Law of Heat Conduction, shown in Equation (5-2). Heat transfer by *convection* involves the mass displacement of a fluid (e.g. air or water), which carries the heated fluid away from the source of heat using the fluid's velocity. Heat transfer by *radiation* involves the emission of electromagnetic radiation from a body, where the energy flux depends on the body's temperature and surface (emissivity).

In COMSOL, the fundamental law of heat transfer is implemented using the first law of thermodynamics. Since internal energy (U) is inconvenient for software to work with, COMSOL uses a modified form of the first law of thermodynamics in terms of absolute temperature (T). The full governing equation [122] is:

$$\left[\rho_d c_p \frac{\partial T}{\partial t}\right] + \rho_d c_p u \cdot \nabla T + \nabla \cdot q = Q$$
(5-1)

, where  $\rho_d$  is the volumetric mass density,  $c_p$  is the specific heat capacity at constant pressure, *t* is time, *u* is the velocity vector, *q* is the conductive heat flux, and *Q* is a heat source (or heat sink). The expression in square brackets denotes the term for the time-dependent case. Fourier's law is of the form shown in Equation (5-2), where  $\kappa$  is the thermal conductivity. If thermal conductivity is a tensor (5-3), as in the case for anisotropic materials (carbon nanotubes for example), then heat flux by conduction is of the form (5-4).

The equation for Fourier's law (with isotropic or anisotropic thermal conductivity) can be inserted back into the conductive heat flux q in Equation (5-1) above.

$$q_i = -\kappa \frac{\partial T}{\partial x_i} \tag{5-2}$$

$$\kappa = \begin{bmatrix} \kappa_{xx} & \kappa_{xy} & \kappa_{xz} \\ \kappa_{yx} & \kappa_{yy} & \kappa_{yz} \\ \kappa_{zx} & \kappa_{zy} & \kappa_{zz} \end{bmatrix}$$
(5-3)

$$q_i = -\sum_j \kappa_{ij} \frac{\partial T}{\partial x_j} \tag{5-4}$$

A surface-to-ambient radiation boundary condition using the Stefan-Boltzmann law was applied to all boundaries. In Equation (5-5),  $\varepsilon$  is the surface emissivity,  $\sigma_{SB}$  is the Stefan-Boltzmann constant, and  $T_{amb}$  is the ambient temperature. A material with an emissivity of 0 is one that emits no radiation off the surface, and one with an emissivity of 1, as is approximately the case for carbon nanotubes, indicates a perfect blackbody.

$$-n \cdot (k\nabla T) = \varepsilon \sigma_{SB} \left( T_{amb}^4 - T^4 \right) \tag{5-5}$$

Lastly, a thermal insulation boundary condition was applied only to the bottom face (copper in the first device, silicon in the second device), which was resting on a vacuum-compatible electrical and thermal insulator in experiments. The boundary condition was simply an inward heat flux of 0.

$$-n \cdot (k \nabla T) = 0 \tag{5-6}$$

### 5.1.2. AC/DC Module Definitions

Simulation of AC/DC electromagnetics in COMSOL involves solving Maxwell's equations given a specified set of boundary conditions. In differential form, they are Maxwell-Ampère's law (5-7), Faraday's law (5-8), and Gauss's laws for electricity (5-9) and magnetism (5-10), respectively. Additionally, the continuity equation (5-11) is used in this module. Thus, we have:

$$\nabla \times H = J + \frac{\partial D}{\partial t} \tag{5-7}$$

$$\nabla \times E = -\frac{\partial B}{\partial t} \tag{5-8}$$

$$\nabla \cdot D = \rho \tag{5-9}$$

$$\nabla \cdot B = 0 \tag{5-10}$$

$$\nabla \cdot J = -\frac{\partial \rho}{\partial t} \tag{5-11}$$
, where *H* is the magnetic field intensity, *J* is the current density, *D* is the electric displacement or electric flux density, *E* is the electric field intensity, *B* is the magnetic flux intensity, and  $\rho$  is the electric charge density. In COMSOL, the **Electric Currents** physics module uses the following equations, where  $Q_j$  is a distributed current source,  $\sigma$  is the electrical conductivity, *E* is the electric field,  $J_e$  is an external current density, and *V* is the electric potential. The expression in square brackets denotes the term for the time-dependent case.

$$\nabla \cdot J = Q_j \tag{5-12}$$

$$J = \sigma E + J_e + \left[\frac{\partial D}{\partial t}\right]$$
(5-13)

$$E = -\nabla V \tag{5-14}$$

All boundaries were given an initial electric potential condition of V = 0. Electric insulation,  $n \cdot J = 0$ , was applied to all boundaries. The hot electrode (bottom copper in the first device, front ITO in the second device) was set to a ground reference, V = 0.

## 5.1.3. Thermoelectric Multiphysics Coupling Definitions

The thermoelectric effect is the conversion of a temperature difference into a potential difference (Seebeck Effect) or the conversion of a potential difference into a temperature difference (Peltier Effect). Therefore, the Heat Transfer and AC/DC COMSOL modules must be coupled together with the appropriate and relevant physical relations. Starting with the heat and electric current flux equations from before, they are now modified to be:

$$q = -\kappa \nabla T + \Pi J \tag{5-15}$$

$$J = -\sigma(\nabla V + \alpha \nabla T) \tag{5-16}$$

, where  $\alpha$  is the Seebeck coefficient,  $\Pi$  is the Peltier coefficient,  $\sigma$  is the electrical conductivity, and  $\kappa$  is the thermal conductivity. Finally, the stationary [and time-dependent] equation for the thermoelectric effect modelled in COMSOL is:

$$\left[\rho_d C_p \frac{\partial T}{\partial t}\right] + \rho_d C_p u \cdot \nabla T + \nabla \cdot (-k\nabla T + \Pi J) = Q$$
(5-17)

## 5.2. Material Parameters Definitions

In order to simulate heating of a solid by laser in COMSOL, a few assumptions were first be made to simplify the model. The electromagnetics of the laser beam were not simulated. Instead, the beam was assumed to be a simple Gaussian-shaped heat source. Also, the effect of the complex refractive index was

modelled using the absorption and reflection coefficients. The following equation (5-27) below has been adapted for use in this model from [124, 125]:

$$Q_{in}(x, y, z) = Q_0(1 - R_c) \cdot \frac{2A_c}{\pi r_x r_y} e^{-\left[\frac{2(x - x_0)^2}{r_x^2} + \frac{2(y - y_0)^2}{r_y^2}\right]} \cdot e^{-A_c(z - z_0)}$$
(5-18)

, where  $Q_{in}$  is the net volumetric heat input,  $Q_0$  is the total (net) incident laser,  $R_c$  is the reflection coefficient, and  $A_c$  is the absorption coefficient. From the previous discussion on the radii of focused the laser beam spot size,  $r_x = r_0 = 1.125$  mm [115], and from the calculations in Chapter 4.2,  $r_y = 0.0375$  mm. The last term is an exponential decay to account for the heat absorption into the material. The beam was incident upon the lower silicon-CNT junction in the first device and upon the front ITO-CNT junction in the second device. The beam spot is the *xy*-plane, where  $z_0$  is the coordinate of the junction surface. Table 7 below shows the room temperature input parameters gathered from references and from experiments.

Parameter	Copper	Silicon	<b>CNT Forest</b>	<b>CNT Forest</b>
			(Literature)	(This Work)
$\alpha (\mu V \cdot K^{-1})$	1.83 [82, 84]	300 [84]	24 (  ) [85]	16.5 (  )
		278 (Ch. 3.3.2)	11 (⊥) [85]	8.0 (⊥) (approx.)
				(Ch. 3.3.2-3.3.3)
$\sigma (S \cdot m^{-1})$	5.79x10 <sup>7</sup> [84]	$4.00 \times 10^4 \ (\rho_m = 0.0025 \ \Omega \cdot cm)$	1800 (  ) [85]	352.2 (  )
	5.998x10 <sup>7</sup> [*]	$4.36 \times 10^4$ (Ch. 3.4.1)	120 (⊥) [85]	97.1 (⊥)
	6.21x10 <sup>7</sup> (Ch. 3.4.1)			(Ch. 3.4.1)
$\kappa (W \cdot m^{-1} \cdot K^{-1})$	400 [*]	148 [*]	0.5 (  ) [85]	
	401 [84]	148 [84]	0.06 (1) [85]	
$c_p (\mathbf{J} \cdot \mathbf{kg}^{-1} \cdot \mathbf{K}^{-1})$	385 [*]	712 [*]	730 [126]	
$\rho$ (kg·m <sup>-3</sup> )	8700 [*]	2300 [*]	60 [85] (2.6 % volume density)	
$\varepsilon_r$ (permittivity)	1 [*]	11.7 [*]	65 [127]	
ε (emissivity)	0.017 [128]	$0.7 (n = 2 \times 10^{19} \text{ cm}^{-3})$	1	
$A_c$ (cm <sup>-1</sup> )		1x10 <sup>4</sup> [129]	0.09x10 <sup>4</sup> [130]	
$R_c$		0.374 (n = 4.15  at  532  nm)	0	
		[131]		

Table 7: Room temperature material parameters, where [] denotes from a reference, [\*] denotes from COMSOL built-in, and () denotes from experiment

The 2D Gaussian exponential from Equation (5-18) is plotted below in the left of Figure 36. The net power transmission coefficient ( $T_P$ ) was 67.5% for the longitudinal conduction device (Chapters 4.2-4.3) and 56.7% for the perpendicular conduction device (Chapter 4.4). For convenience,  $Q_0$  is defined as the setpoint laser power set at the laser control panel ( $Q_{SP}$ ) multiplied by the transmission coefficient ( $T_P$ ).

$$Q_0 = Q_{SP} * T_P \tag{5-19}$$

The right of the same figure shows a surface temperature plot when 405 mW of laser power was incident upon the longitudinal conduction device from Chapter 4.3. It can be seen that under a temperature gradient of 2.6 K was maintained at steady state.



Figure 36: (left) 2D Gaussian plot approximation of laser beam shape, (right) surface temperature plot under incident laser power of  $Q_0 = 405 \text{ mW}$ 

#### 5.3. Longitudinal Conduction Device Model

Based on the experiments described in the previous chapter, the thermoelectric device geometry was drawn in COMSOL to scale, and is shown below in Figure 37 with the following dimensions: copper ( $A = 25x25 \text{ mm}^2$ ,  $t_h = 1.5 \text{ mm}$ ), silicon ( $A = 6x6 \text{ mm}^2$ ,  $t_h = 0.5 \text{ mm}$ ), and CNT ( $A = 6x6 \text{ mm}^2$ ,  $t_h = 0.7 \text{ mm}$ ).



Figure 37: Perpendicular conduction device schematic sketched in 3D

To study the longitudinal conduction device in COMSOL, four models were constructed with increasing levels of complexity. The differences between the models are summarized below in Table 8. Model 1 assumed all material properties were those measured at room temperature as reported in the literature. The electrical conductivity of silicon was calculated from the median wafer resistivity reported by the manufacturer. Model 2 replaced all the material property values with the room temperature experimental measurements if available, which were the Seebeck coefficient of silicon and CNTs, and the electrical conductivity of all three materials. Model 3 was almost identical to Model 2 with the exception that a constant thermal conductivity of CNTs was used as a fitting parameter for each laser power (it was varied at each laser power until the simulated value of the induced voltage matched the value measured

experimentally). It was assumed to be an order of magnitude larger in the longitudinal direction compared to the perpendicular directions. The thermal conductivity was tuned so that the simulated steady-state induced voltage difference equaled the experimental steady-state induced voltage difference to within a precision of  $\pm 1 \mu$ V. Lastly, Model 4 introduced the temperature-dependent material parameters, where the Seebeck coefficients of silicon and CNTs were measured as functions of temperature in this work. Again, thermal conductivity of CNTs was a fitting parameter. Tables of the CNT thermal conductivity, hot and cold junction temperatures, temperature difference, maximum temperature, and voltage difference are shown in Appendix B for reference.

Parameter	Model 1 (RT ref.)	Model 2 (RT exp.)	Model 3 (RT, exp.)	Model 4 ( $f(T)$ )
$\alpha_{Cu}$	Constant	Constant (ref)	Constant (ref)	$\alpha(T)$ (ref)
$\sigma_{Cu}$	Constant	Constant	Constant	$\sigma(T)$ (ref)
К <sub>Cu</sub>	Constant	Constant (ref)	Constant (ref)	$\kappa(T)$ (ref)
$\alpha_{Si}$	Constant	Constant	Constant	$\alpha(T)$ (exp)
$\sigma_{\rm Si}$	Constant	Constant	Constant	$\sigma(T)$ (theoretical)
κ <sub>Si</sub>	Constant	Constant (ref)	Constant (ref)	$\kappa(T)$ (ref)
$\alpha_{\rm CNT}$	Constant	Constant	Constant	$\alpha(T)$ (exp)
$\sigma_{CNT}$	Constant	Constant	Constant	$\sigma(T)$ (ref)
K <sub>CNT</sub>	Constant	Constant (ref)	κ, tuning parameter	$\kappa(T)$ , tuning parameter

Table 8: Comparison of COMSOL model material properties

#### 5.3.1. Model 1: Room Temperature Reference Material Parameters

For the first model, room temperature material parameters from Table 7 were inputted into the COMSOL model. The incident laser power was swept in the range of 6.8 - 472.5 mW as was performed in the experiments. The steady-state results are plotted below in Figure 38. In part (a), the simulated voltage as a function of setpoint laser power is shown in red X's and the experimental voltage is shown in blue O's. It can be seen that the simulated voltage was in a similar order of magnitude as the experimental voltage.

However, in experiments, there was a noticeable threshold laser power (67.5 mW) before a non-zero steady-state voltage could be measured, whereas a voltage was induced at any laser power in this model. We believe that in experiments at low laser powers (low temperatures), the thermal conductivity of CNTs was much greater than the conductivity at higher temperatures, indicative of a fall-off with temperature. At low temperatures, the lower silicon and the CNT forest were believed to have similar, but opposite in sign, induced voltage contributions, so a very small net voltage was induced. However, this first model assumed a constant CNT thermal conductivity, as shown in part (d) as a function of average temperature, so it is quite unrealistic and therefore needs to be refined.

As previously discussed in Chapter 3.3.1, because the thermal conductivity of CNTs in general is much lower than that of copper or silicon, its Seebeck coefficient will dominate the effective coefficient of the entire device, shown in part (c) as a function of average temperature. If the CNT Seebeck coefficient is too small, then the simulated induced voltage difference can be underestimated and this could explain why the slope of  $\Delta V$  vs.  $Q_{SP}$  is shallower in simulation. The effective Seebeck coefficient was a constant 24  $\mu$ V/K and equal to that of the CNT Seebeck coefficient. Alternatively, an overestimated inputted thermal conductivity, shown in part (d), can result in an underestimated temperature difference, shown in the bottom of part (b) as a function of laser power. This also has the effect of an underestimated voltage difference.

Since all material parameters were assumed to be constant with temperature, increases in the junction temperature difference resulted in proportional increases in induced voltage difference across the two junctions. In part (b), it may be initially intuitive from this simple model that the hot and cold junction temperatures, as well as the average and maximum temperature, should increase proportionally with increasing laser power. However, all open-facing boundaries underwent surface-to-ambient radiation with a  $T^4$  dependence, so this is why those temperatures were tapering off with increasing setpoint laser power.



Figure 38: Model 1 (a) induced voltage difference from simulation (red X's) and experiment (blue O's), (b) (top) hot junction (red X's), cold junction (blue  $\Box$ 's), maximum temperature (black O's), (bottom) temperature difference as functions of incident laser power, (c) effective Seebeck coefficient, (d) inputted longitudinal (red X's) and perpendicular (blue O's) CNT thermal conductivity as functions of average temperature

## 5.3.2. Model 2: Room Temperature Experimental Material Parameters

The second model was nearly identical to the first model, but with experimental room temperature material parameters inputted when available. Therefore, we shouldn't expect much of a difference in the results, which are shown below in Figure 39. In part (a), the induced voltage difference from the simulations was now smaller in magnitude and further away to that from experiment. This is because the Seebeck coefficient of CNTs measured experimentally (shown in part (c) as an effective 16.5  $\mu$ V/K) was smaller than those reported in the literature (24  $\mu$ V/K from before). Because the inputted CNT thermal conductivity in part (d) was unchanged from Model 1, the thermal behaviour of the system was also unchanged. Therefore, the temperature behaviour shown in part (b) was unchanged. If the effective  $\alpha$  is smaller and  $\Delta$ T is unchanged, then  $\Delta$ V must decrease accordingly. Since we know that this was the actual Seebeck coefficient of our device, rather than one assumed from literature, we can conclude that the temperature gradient in this model was underestimated due to an overestimated thermal conductivity of CNTs.



Figure 39: Model 2 (a) induced voltage difference from simulation (red X's) and experiment (blue O's), (b) (top) hot junction (red X's), cold junction (blue  $\Box$ 's), maximum temperature (black O's), (bottom) temperature difference as functions of incident laser power, (c) effective Seebeck coefficient, (d) inputted longitudinal (red X's) and perpendicular (blue O's) CNT thermal conductivity as functions of average temperature

## 5.3.3. Model 3: Room Temperature Experimental Material Parameters, Tuned $\kappa_{CNT}$

In Model 3, the same experimental material parameters were inputted when available. This time, the longitudinal thermal conductivity of CNTs was tuned so that the simulated steady-state induced voltage difference equaled the experimental value to a precision of  $\pm 1 \mu V$ . The perpendicular CNT thermal conductivity was assumed to be an order of magnitude smaller, which is similar to what is reported in the literature [85, 107]. From the previous model, the simulated voltage difference below 200 mW of incident laser power was too large given a longitudinal CNT thermal conductivity of 0.5 W·m<sup>-1</sup>·K<sup>-1</sup>. The thermal conductivity was underestimated, which resulted in a higher temperature gradient between the two junctions and therefore a higher than desired voltage difference. On the other hand, the simulated voltage difference beyond 200 mW of incident laser power was too small, so the thermal conductivity was overestimated in that range.

Since non-zero steady-state voltages were measured only above 67.5 mW of incident laser power, the 6.8-47.3 mW laser powers were not simulated for this model and the next one. In part (c) of Figure 40 below, we can see that the effective Seebeck coefficient of the device was unchanged since the CNT Seebeck coefficient was also unchanged. As mentioned before, at each value of laser power, the thermal conductivity of nanotubes was varied until the simulated voltage closely matched the value measured experimentally. The tuned thermal conductivity shown in part (d) as a function of average temperature exhibited a fall-off with increasing temperature. At around 360 K and corresponding to an incident laser power of 67.5 mW, the thermal conductivity obtained in this manner was high. At a value of 5 W·m<sup>-1</sup>·K, the  $\Delta$ T was sufficiently small so that the  $\Delta$ V was also sufficiently small (< 1.5  $\mu$ V) to match the experimental result. However, beyond 200 mW of incident laser power, the thermal conductivity had to fall below 0.5 W·m<sup>-1</sup>·K<sup>-1</sup>, which was the conductivity used in the previous models. Compared to before,  $\Delta T$  in part (b) was larger, so  $\Delta V$  in part (a) was also larger and now matched with the experiment. The original explanation for the "Heat Trap" effect was partially based on a decrease in thermal conductivity with increase in temperature [30, 132]. Therefore, the behaviour obtained here is very significant, in that it represents an independent confirmation of that mechanism for the "Heat Trap" effect.



Figure 40: Model 3 (a) induced voltage difference from simulation (red X's) and experiment (blue O's), (b) (top) hot junction (red X's), cold junction (blue  $\Box$ 's), maximum temperature (black O's), (bottom) temperature difference as functions of incident laser power, (c) effective Seebeck coefficient, (d) tuned longitudinal (red X's) and perpendicular (blue O's) CNT thermal conductivity as functions of average temperature

## 5.3.4. Model 4: Temperature-Dependent Material Parameters, Tuned KCNT

Temperature-dependent model parameters from a mixture of experimental and reference data were used with piecewise cubic interpolation functions. We assumed here that the Seebeck coefficient of CNTs does not change significantly beyond around 400 K, as reported previously [87, 88], so extrapolation was set to a constant. Although the experimental measurement of the temperature-dependent Seebeck coefficient of silicon was not performed to very high temperatures, we can safely assume a continuous linear relationship, as reported previously [86]. All other extrapolation was performed using a nearest function approximation, where COMSOL automatically numerically fits a polynomial for information beyond the inputted data.

Similar to Model 3, tuning of the CNT thermal conductivity was performed assuming an order of magnitude greater conduction longitudinally. The steady-state voltage and temperature results are shown below in Figure 41. In part (c), the effective Seebeck coefficient was much higher now due to the temperature-dependent CNT coefficient increasing up to a constant 54  $\mu$ V/K at 400 K and higher. With a

higher Seebeck coefficient compared to Model 3, a smaller temperature gradient in part (b) was required to induce the same voltage in part (a). Therefore, CNT thermal conductivity in part (d) was higher than in Model 3, but with the same fall-off behaviour with increasing temperature. In this final model, the cold junction temperatures shown in blue  $\Box$ 's of part (b) reached a maximum of 518 K (245 °C) at the highest incident laser power. In experiments, the bottom face of the bottom copper electrode was in direct contact with the PEEK insulator, which, at steady-state, would be at the same temperature as the cold junction. Since these simulated temperatures were much below the melting point of PEEK (334-350 °C [83]) and the insulator was not observed to be melting in the experiments, we believe the simulations to be realistic.



Figure 41: Model 4 (a) induced voltage difference from simulation (red X's) and experiment (blue O's), (b) (top) hot junction (red X's), cold junction (blue  $\Box$ 's), maximum temperature (black O's), (bottom) temperature difference as functions of incident laser power, (c) effective Seebeck coefficient, (d) tuned longitudinal (red X's) and perpendicular (blue O's) CNT thermal conductivity as functions of average temperature

The voltage and temperature difference can also be studied as a function of time, as shown below in Figure 42. Upon 337.5 mW of incident laser power, the temperature gradients across copper shown in part (a), and silicon and the CNT forest shown in part (b) were studied up to 3 seconds. As predicted earlier in Chapter 4.3, the temperature gradient across the bottom copper was nearly instantaneously negative and larger in magnitude compared to the upper copper electrode. In part (c), the induced voltage difference

across copper contributed a negligibly small voltage to the net voltage, shown in black in part (d). In part (b), we see that the bottom silicon and the CNT forest had nearly instantaneous, large temperature gradients across them, while the gradient across the top silicon was negligibly small. The gradient across the CNTs was growing over time and, as a result, the induced voltage across the CNT in part (d) was slightly larger in magnitude than that of the bottom silicon. The net induced voltage in part (d) is the sum of each of the contributions at each time point. Beyond 2.6 seconds, the positive contributions were larger than the negative contributions, so a net positive voltage appeared.



Figure 42: Time-dependent Model 4 temperature difference across (a) copper, (b) silicon, CNT, and entire device, induced voltage difference across (c) copper, (d) silicon, CNT, and entire device under incident laser power of  $Q_0 = 337.5$ mW

The net temperature differences ( $T_{16}$ ) and induced voltage differences ( $V_6$  or  $V_{net}$ ) can be studied as a function of time on a longer time scale for the same incident laser power of 337.5 mW. This is shown below in Figure 43 with a 10 second step size. In part (a), the temperature gradient across the bottom silicon (red) is smaller than the gradient across the CNT forest (green), where the gradient across the top silicon (blue) is almost negligible. The overall net temperature difference across the entire device, shown in black, was slightly smaller than that across just the CNTs. In part (b), we can see the effect of the temperature gradients in the induced voltage differences across the same materials. Although the top silicon had a very small

temperature gradient, the large Seebeck coefficient of silicon still meant there was a fair amount of positive voltage contribution. The voltage across the bottom silicon was fairly large, negative, and growing in magnitude. However, although the CNTs had a relatively lower Seebeck coefficient compared to silicon, the larger temperature gradient across the CNTs meant there was a large, positive, and growing voltage across them. We can see that the sum of the green and blue curves was larger than the red curve. Therefore in black, we can clearly see that the net induced voltage across the device was positive.



Figure 43: Time-dependent Model 4 (a) temperature difference across silicon, CNT, and entire device, (b) induced voltage difference across silicon, CNT, and entire device under incident laser power of  $Q_0 = 337.5$ mW

Figure 44 below is the time-dependent net temperature difference and net induced voltage difference behaviour of the entire device under varied setpoint laser powers. The time scale plotted below runs up to 0.5 second (a, c) with a 0.001 second step size, and up to 100 minute (b, d) with a 10 second step size. In parts (a) and (b), the net temperature gradients were always positive, meaning the lower part of the device was always warmer than the upper part.

In the 0.5 second time scale of the induced voltage in part (c), we observed the same initial rapid dip to negative voltages that was previously seen in experiments The dip grew in magnitude with increasing laser power in the same way as in experiments. It was unclear why there was an additional dip and spike in voltage under irradiation from the highest two powers, but perhaps we can suggest that there was close competition between the negative voltage contributions from the lower silicon with the positive voltage contributions from the CNT forest. Nevertheless, we observed a turning point at 0.3 second where it was clearly seen that the high laser powers induced a larger negative voltage. The voltage crossover point was around 2.5-3 second for all laser powers, whereas 100-120 second was observed in experiments. From before, we know that the thermal effects based on Equations (4-2) through (4-4) and observed in simulation assumed Ohmic electrical contact and perfect thermal contact between materials. This discrepancy in the crossover time suggests that electrical and thermal resistances were definitely present in the experimental

device, which can be challenging to simulate. Nevertheless, the trend of a dip to negative voltages increasing in magnitude with increasing laser power was observed both in experiments and in simulation.

Over a span of 100 minutes, the induced voltage shown in part (d) was seen to steadily increase towards larger and larger values and eventually settle at a steady-state value beyond this time scale. The simulation could be extended to an even longer time scale, but this comes at the expense of computation time. The local maximum in output voltage in the 5-10 minute time mark was primarily due to the identical fluctuations in the temperature, as shown in part (b). The local maxima in temperature differences and subsequent dips beyond suggest that either the temperature gradient across the CNT forest decreased slightly and/or the temperature gradient across the bottom silicon decreased. In both cases, the effect was a decrease in net induced voltage. Nevertheless, the net temperature gradient increased again after 20-30 minutes for all laser powers, so voltage also increased.



Figure 44: Time-dependent Model 4 (a, b) net temperature difference across entire device, (c, d) net induced voltage difference across entire device with varying incident laser power  $Q_0$ 

While not performed in the experiment, the x and y position of the laser were also varied in simulation to study the effects on the induced voltage. Shown below in the left and right of Figure 45 are the voltage

changes when the centre of the laser was moved relative to the absolute centre of the CNT forest sidewall. Intuitively, moving the laser along *x* showed symmetry with respect to the original position. As the laser was moved either to the left or to the right, more and more of the heat spot spread to the peripheries. At distances of  $x = \pm 3$  mm, only half of the laser spot was incident upon the CNT forest sidewall.

Moving the laser along y showed a similar symmetry trend. At the lowest end at y = -0.8 mm, the laser essentially only irradiated the silicon, which, if performed in experiments, would reflect back most of the laser light. Whatever marginal heat was absorbed was easily drawn away by the larger lower copper electrode. A similar situation occurred at the highest end at y = 0.8 mm. As the laser was moved vertically closer to the centre of the forest, a maximum voltage was induced at a distance of 0.3 mm away in either direction. At this distance, the elliptical-shaped heat flux was entirely incident on only the CNT sidewall (no beam spot on silicon) and the absolute furthest it can be away from the centre of the forest. In experiments, a distance of approximately -0.35 mm was used, as indicated by the green star, as this was the distance to which the beam spot was centred on the junction between silicon and CNTs. For future experiments, the laser beam should be steered in a more careful and precise manner in order to maximize the output voltage of the thermoelectric device.



Figure 45: Steady-state Model 4 induced voltage difference under incident laser power of  $Q_0 = 337.5 \text{ mW}$  aimed at varying (left) x-coordinates and (right) y-coordinates, where the green star indicates the experimental coordinate

## 5.4. Perpendicular Conduction Device Model

Similar to the previous model, the perpendicular conduction device described in Chapter 4.4 was drawn in COMSOL to scale and shown below in Figure 46 with the following material dimensions: ITO (A = 10x4 mm<sup>2</sup>,  $t_h = 0.7$  mm), silicon (A = 6x6 mm<sup>2</sup>,  $t_h = 0.5$ mm), and CNT (A = 6x6 mm<sup>2</sup>,  $t_h = 0.7$  mm). The 2D Gaussian exponentially-decaying heat flux from Equation (5-18) was also used in this model, and the  $z_0$ coordinate where the beam was incident was set to the location of the exact junction between the front ITO electrode and the CNT forest sidewall. This coordinate was chosen since in experiments, the laser travels through the transparent ITO window and heats up the junction, rather than just the front ITO face. To take the optical transmission losses off all experimental optical components and through the front ITO into account, the transmission coefficient was set to 56.7 % (from Chapter 4.4). Table 9 below lists the relevant material parameters, where the simulation model assumed the room temperature reference values of ITO that were available. Similar to before, all surfaces have a surface-to-ambient radiation heat transfer boundary condition, except for the bottom face, which was thermally insulated. The front ITO electrode was set at a ground reference point and voltage was measured at the back ITO electrode.

Parameter	ITO
$\alpha (\mu V \cdot K^{-1})$	81.1 [133]
$\sigma$ (S·m <sup>-1</sup> )	$4.63 \times 10^5$ (12 Ω/sq, $t = 180$ nm)
$\kappa (W \cdot m^{-1} \cdot K^{-1})$	10.2 [134]
$c_p \left( \mathbf{J} \cdot \mathbf{kg}^{-1} \cdot \mathbf{K}^{-1} \right)$	340 [135]
$\rho$ (kg·m <sup>-3</sup> )	6800 [136]
$\varepsilon_r$ (Permittivity)	9.3 [137]
ε (Emissivity)	0.25 [138]
$A_c (\mathrm{cm}^{-1})$	664 [139]
$R_c$	$0.104 \ (n = 1.95 \text{ at } 532 \text{ nm}) \ [140]$

*Table 9: Indium tin oxide room temperature material parameters* 



#### 5.4.1. Model 5: Perpendicular Conduction with ITO Electrodes

From the thermal conductivity of CNTs as a function of average temperature in part (d) of Figure 41, a piecewise cubic interpolation curve can be fit, alongside nearest function extrapolation for higher temperatures. Therefore, temperature-dependent interpolation curves for the Seebeck coefficient, electrical conductivity, and thermal conductivity for both silicon and CNTs were inputted into this model. Figure 47 below shows the surface temperature (left) and potential (right) plots upon 283.5 mW of incident laser power irradiation, where the device dimensions are in units of mm. In the surface temperature plot, the hot

spot on the CNT forest can be seen to extend longitudinally towards the top of the CNT forest and also in the other directions perpendicularly, but to a lesser extent. By arranging the ITO contact electrodes in this configuration, we have successfully taken advantage of the anisotropic thermal conductivity of CNTs and created a large enough temperature difference (~24 K) between the two CNT-ITO junctions to induce a thermoelectric voltage (~4.6 mV) at this laser power.

We would intuitively think that upon irradiance by such high laser powers that the "Heat Trap" effect would arise and the temperature gradient should be much larger. However, we believe that the ITO, with a thermal conductivity of  $10.2 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at room temperature [134], was acting like an undesirable heat sink at the hot junction and drawing away much of the hot junction temperature. We believe this may be dominating over or completely overshadowing any of the benefits of the "Heat Trap" effect. Perhaps a different transparent conductive oxide thin film electrode with a lower thermal conductivity would be a better choice for a future device, so that an even larger temperature gradient could be sustained.



Figure 47: Model 5 (left) surface temperature and (right) surface potential under incident laser power of  $Q_0 = 283.5$  mW

The laser was aimed at the absolute centre of the CNT forest sidewall both in experiments and in simulation. Shown below in Figure 48 is the simulated steady-state temperature profile along the *z*-axis starting from the front ITO electrode (solid red), into the CNT forest (dashed green), and lastly through the back ITO electrode (dotted blue), again under an incident laser power of 283.5 mW. The exponential absorption of heat into the CNT forest, shown as an exponential decrease in temperature into the depth the CNT forest, can be seen in the dashed green line. Upon first glance, one would assume that the temperature should be hottest at the exact junction between the front ITO and the CNT forest where the laser was incident, or in other words, at the intersection of the red and green curves below. However, the location of the highest temperature was actually about 0.25 mm deeper into the forest. Again, we believe that ITO was acting like an undesirable heat sink at the hot junction and causing this effect.



Figure 48: Model 5 temperature along z-axis through front ITO (solid red line), through the CNT forest (dashed green line), and through back ITO (dotted blue line) under incident laser power of  $Q_0 = 283.5$  mW aimed at absolute centre of CNT sidewall

A table of the steady-state hot and cold junction temperatures, temperature difference, maximum temperature, and voltage difference for this model is shown in Appendix C. The average output voltage from experiment is plotted in the blue O's of part (a) of Figure 49 below. Using a combination of experimental results from a different device, alongside Model 4 simulation results to determine the thermal conductivity of CNTs, the simulated steady-state voltage of this new device was modelled and shown in red X's in the same plot. Without tuning any parameters, the simulated voltage matched very well with the experiment. This is a truly remarkable result that serves as a good confirmation of the parameters obtained previously. Shown in part (b) on top are the hot junction, cold junction, and maximum temperature, and on bottom is the temperature difference. Compared to the previous device, the junction temperatures in this new device were larger. As discussed previously, the Seebeck coefficient and electrical conductivity of CNT forests increased with temperature and the thermal conductivity decreased with temperature. All three of these trends at higher temperatures are beneficial towards enhancing the figure-of-merit and therefore the device efficiency.

In this configuration, we intentionally placed the ITO contact electrodes in such a manner that heat must conduct in the perpendicular direction. Although the thermal conductivity of CNTs can be up to two orders of magnitudes smaller in the perpendicular direction, this simulation was run with a more conservative estimate of a one order of magnitude difference. As a result, this had an effect of a larger temperature gradient, shown in the bottom of part (b), compared with the previous device. Lastly, the effective Seebeck coefficient of the entire device, shown in part (c), was also larger compared to the previous device and in the range of a few hundred  $\mu V/K$ . While ITO was electrically connected in series with the CNT forest (perpendicularly), the forest was also connected to its silicon substrate. Therefore, ITO was in series with the parallel combination of silicon and CNTs. Equations (3-1) through (3-6) are not

immediately effective to predict the effective Seebeck coefficient. However, it is clear that the Seebeck coefficient was not dominated solely by that of CNTs this time, but had some weighting from the silicon and ITO, both of which have much higher coefficients than MWCNTs.



Figure 49: Model 5 (a) induced voltage difference from simulation (red X's) and experiment (blue O's), (b) (top) hot junction (red X's), cold junction (blue  $\Box$ 's), maximum temperature (black O's), (bottom) temperature difference as functions of incident laser power, (c) effective Seebeck coefficient, (d) input longitudinal (red X's) and perpendicular (blue O's) CNT thermal conductivity as functions of average temperature

While not performed in experiments, the *x* and *y* position of the laser was once again varied in simulation to study the effects on the induced voltage. Shown below in the left and right of Figure 50 are the steady-state induced voltage changes when the centre of the laser was moved relative to the absolute centre of the CNT forest sidewall. Moving the laser along *x* showed symmetry around the centre position at x = 0 mm. Just like before, as the laser was moved either to the left or to the right of the centre, more and more of the heat was lost as it no longer irradiated the CNT forest. At distances of  $x = \pm 3$  mm, only half of the laser spot was incident upon the CNT forest sidewall.

Moving the laser along y showed a different trend. At the lowest end at y = -0.3 mm, the laser was mostly irradiating the silicon-CNT junction, whereby heat was more easily carried away by silicon with its

high thermal conductivity ( $\kappa = 148 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at room temperature [84]). The temperature gradient was lower and therefore the induced voltage was also lower relative to the original centre position. As the laser was moved vertically upwards, more and more heat was retained by the CNT forest ( $\kappa < 2 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  at *T* > 400 K). Due to a larger temperature gradient, the voltage difference was also larger. Steady-state induced voltage reached a maximum at a distance of 0.2 mm above the central position, and then decreased. We believe that at the maximum, the laser was at an optimal position so that heat drawn away into the silicon pathway and heat radiated away from the top CNT surface were both minimized, so the temperature gradient was at a maximum. At the highest position at *y* = 0.3 mm, too much heat was radiated away from the top surface. Thus, the temperature gradient and voltage difference were both low in comparison.



Figure 50: Steady-state Model 5 induced voltage difference under incident laser power of  $Q_0 = 283.5 \text{ mW}$  aimed at varying (left) x-coordinates and (right) y-coordinates, where the green star indicates the experimental coordinate

#### 5.4.2. Model 5: Effect of Substrate and Material Properties

In the perpendicular conduction device, the underlying silicon substrate may be detrimental towards the overall device efficiency. Intuitively, heat generated at the front ITO-CNT junction will be drawn longitudinally along the length of the nearest nanotubes, more so than perpendicularly between adjacent nanotubes. Heat reaching the exposed top of the forest will be dissipated by radiation. Heat reaching the root of the forest will be drawn into the silicon pathway and, due to the high thermal conductivity of silicon, the silicon will act as a thermal shunt and effectively reduce the temperature difference between the two ITO-CNT junctions.

It is not immediately clear how much of the induced photo-thermovoltage in experiments was due to the silicon substrate, which has a high Seebeck coefficient. In order to isolate the effects of the underlying silicon substrate, it was removed from the simulation model completely, while all other materials and parameters were held constant. The induced voltage as a function of incident laser power is shown in part (a) of Figure 51 below, where the red X's represent the simulated voltage with silicon and the blue O's

represent the simulated voltage without the silicon substrate. Without the substrate, the voltage was a few mV higher than with silicon. As well, the shape and trend of the curve was not matched with that from experiment (black  $\diamond$ 's). From this, we can conclude that the experimental voltages were indeed a consequence of a combination of the thermal and electrical properties of both the CNT forest and its silicon substrate.

Shown in part (d) of the same figure are the temperature profiles of the hot side, cold side, and maximum temperatures on the top, and the temperature difference on the bottom as functions of incident laser power without the underlying silicon substrate. Without the substrate, the low thermal conductivity of the CNT forest in the perpendicular direction promoted a much higher temperature gradient than in the configuration with the substrate, as shown in part (b) and, consequently, a slightly higher induced voltage.



Figure 51: Model 5 (a) induced voltage difference from simulation with silicon substrate (red X's), with quartz substrate (green  $\Box$ 's), without a substrate (blue O's), from experiment with silicon substrate (black  $\diamond$ 's) as functions of incident laser power, (b-d) (top) hot junction (red X's), cold junction (blue  $\Box$ 's), maximum temperature (black O's), (bottom) temperature difference as functions of incident laser power with silicon substrate, with quartz substrate, and without a substrate

Since it is apparent that the silicon substrate played a detrimental role in drawing away heat from the hot junction, a wise choice would be to remove it from future thermoelectric devices completely. However, in practice, it is relatively challenging to fabricate a device with a free-standing CNT forest. Not only is the material very lightweight and prone to "flying away," but due to the mostly empty space of the forest, it is highly compressible and difficult to attach electrodes to. It is, however, feasible to deposit the thin film catalyst (described in Chapter 2.2) onto an insulator, such as quartz. In simulation, the silicon substrate in Model 5 was directly replaced with quartz, which was then excluded from the AC/DC physics module. The room temperature material properties of quartz are as follows:  $\rho_d = 2210 \text{ kg} \cdot \text{m}^{-3}$ ,  $c_p = 730 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ ,  $\kappa = 1.4 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ ,  $\varepsilon = 0.93$ . The induced voltage as a function of incident laser power is shown in green  $\Box$ 's in part (a) of the same figure. Rather than exponentially growing in magnitude with increasing incident laser power, the voltage remained relatively linear in this range. Below around 180 mW of power, the voltage was higher with quartz than with silicon, but beyond this value, the situation was reversed.

Comparing the temperature profiles between the device with silicon in part (b) and with quartz in part (c), the hot side temperatures were similar. However, due to the much lower thermal conductivity of quartz, the cold side temperatures for the device with quartz were much lower than with silicon. One would initially assume that a high temperature gradient would result in a high induced voltage. However, quartz, being an insulator, does not provide any voltage, whereas silicon, with its high Seebeck coefficient, did so. Therefore, although quartz helped promote a high temperature gradient, the relatively small Seebeck coefficient of the CNT forest in the perpendicular direction was not able to harness the temperature gradient to induce a voltage to an appreciable amount. Compared with the device without a substrate in part (d), the temperature gradient with quartz was smaller because, although it has a low thermal conductivity, the thermal conductivity of quartz was still higher than the perpendicular CNT conductivity. Some incident heat was shunted into the quartz pathway, although much less than if the substrate was silicon. From this, we can conclude that if one wishes to maximize the induced voltage using the same MWCNT forests, not only does the device have to be able to sustain a high effective temperature gradient (as it was with quartz in simulation), but it is beneficial to have a high effective Seebeck coefficient (as it was with silicon). An investigation into a more ideal substrate, i.e. one with a low thermal conductivity and high Seebeck coefficient, would be necessary for future simulations and experiments. Alternatively, a very low thermal conductivity insulator could be used as a support for CNT forests with an optimized Seebeck coefficient.

Shifting our focus back to the original configuration with the silicon substrate, we now observe the thermal effects of the attached silicon and ITO pieces. Since both of these materials have relatively high thermal conductivities, it was believed that they undesirably drew away heat from the hot side of the CNT forest. Shown below in Figure 52 are the temperature cross-sections of the CNT forest along the *x*-direction

in part (a) (from left to right on the hot face, centred vertically half way up the forest), along the *y*-direction in part (b) (from bottom to top on the hot face, centred horizontally in the middle of the forest), and along the *z*-direction in part (c) (from the hot face to the cold face, centred in the absolute middle of the forest). The inset schematic in the same figure shows these directions as white arrows. In each of these directions, a cross-sectional temperature slice was taken for various configurations: the original CNT configuration with silicon and ITO (solid red lines), with only ITO (dotted green lines), with only silicon (dot-dashed blue lines), and a bare CNT forest (dashed black lines).

In part (a), there was symmetry in the *x*-direction for all configurations. The temperature at x = 3 mm was the exact centre of the hot side CNT sidewall or, in other words, the exact location at which the laser was centred and therefore the point of maximum temperature. This was the same temperature at y = 0.35 mm in part (b) and z = 0 mm in part (c). Between the four configurations, the maximum temperature was smallest when both silicon and ITO were in contact with the CNT forest, since both materials drew away heat from the hot junction. With ITO and no silicon, the overall temperature was elevated by over 100 K. This was because in the presence of silicon, heat applied at the front junction was easily drawn away into the silicon pathway (high thermal conductivity) and distributed throughout the CNT forest. With silicon and no ITO, the situation was similar to the original configuration. However, the low perpendicular thermal conductivity of the CNTs maintained a high temperature at the peripheries was much lower than at the centre since it was not spread out and drawn into the ITO pathway. Finally, for a bare CNT forest, the temperature gradient in this direction was the largest among the four configurations. Again, this was due to the low perpendicular thermal conductivity of the CNTs causing the majority of the heat to be confined within the heated region.

Along the y-direction in part (b), there was near-symmetry about the centre of the forest for the original configuration. Since the longitudinal thermal conductivity of the CNTs is higher in this direction compared to the perpendicular direction, heat was drawn into the silicon pathway fairly easily, so the temperature at the top of the forest at y = 0.7 mm was slightly higher. For the configuration with only ITO, there was also near-symmetry, but the temperatures were naturally higher. This time, the temperature at the top of the forest was colder than at the bottom. The top surface released heat by radiation, whereas the bottom of the forest was thermally insulated. However, with only silicon, the bottom of the forest was over 50 K colder than the top of the forest due to the underlying silicon drawing away heat from the bottom of the forest. The CNT forest on its own was relatively constant in temperature along the y-direction with only 2 K higher temperature at the middle of the forest; there was no material to release the incident heat into. Due to the one order of magnitude larger longitudinal conductivity compared with the perpendicular conductivity, the

majority of the incident heat conducted along this direction. The temperature gradient in the *y*-direction was therefore much smaller than that in the *x*-direction shown in part (a).

Along the *z*-direction in part (c), naturally, all configurations were hotter at the side of the forest exposed to laser irradiation than at the back of the forest. As discussed before, the hottest *z*-coordinate of the original configuration was around 0.2 mm into the forest. This was explained by the fact that the front ITO electrode served as an undesirable heat sink and lowered the temperature of the hot junction. With only ITO, there was also a maximum in temperature into the forest; the temperature gradient was the highest of all the configurations at around 300 K. With only silicon, the situation was similar to the original configuration, but with a lower cold junction temperature. Lastly, for a CNT forest on its own, the temperature was greatest at the front face of the forest and decayed exponentially, as expected from the model of the laser source used in these simulations (Equation (5-18)). Its temperature gradient was not as high as in the configuration with ITO electrodes. Although the front ITO reduced the hot junction temperature, the back ITO also effectively reduced the cold junction temperature more than if the ITO was not in place. These results show that there was definitely an effect of the underlying silicon substrate and of the attached ITO electrodes.



Figure 52: Model 5 temperature along (a) X, (b) Y, (c) Z with CNT, silicon, and ITO (solid red line), CNT and ITO (dotted green line), CNT and Si (dot-dashed blue line), no silicon and ITO (dashed black line) under incident laser power of  $Q_0 = 283.5$  mW

The longitudinal and perpendicular thermal conductivity of the forest were varied to a wide range of values in order to gain insight into the sensitivity of the device to its material parameters. In Figure 53 below, the longitudinal thermal conductivity of the CNTs was varied between 0.01 - 100 W·m<sup>-1</sup>·K<sup>-1</sup> (constant with temperature), while the perpendicular conductivity was assumed to be an order of magnitude smaller as before. Shown in black  $\diamond$ 's is the average induced voltage from experiment. Naturally, at lower and lower thermal conductivities, the nanotubes were able to prevent more heat from escaping upwards towards the top of the forest and radiating, and downwards towards the silicon and away from the hot junction. Higher temperature gradients were maintained at lower thermal conductivities, so the induced voltage was enhanced.



*Figure 53: Model 5 induced voltage difference from simulation (coloured O's) and from experiment (black*  $\diamond$ *'s) with varied*  $\kappa_{CNT}$ 

However, within a 3-order-of-magnitude variation in thermal conductivity, surprisingly there was not much of a change in the induced voltage. To further study this, a cross-section of the temperature profile along the *z*-direction was taken for the original configuration, with the silicon removed, and with the ITO removed, shown as parts (a), (b), and (c) respectively in Figure 54 below. The longitudinal thermal conductivity of the CNT forest was once again varied between 0.01 - 100 W·m<sup>-1</sup>·K<sup>-1</sup>, which was one order of magnitude larger than the perpendicular conductivity. Consistent within all three configurations, there was an observed maximum in temperature around z = 0.2 - 0.5 mm into the forest. The maximum increased with decreasing CNT thermal conductivity. The temperature difference along *z*, i.e. the difference in temperature between z = 0 mm and z = 4.6 mm, is shown in part (d) as a function of longitudinal CNT thermal conductivity for the three configurations: the original CNT configuration with silicon and ITO (red X's), with only ITO (green  $\Box$ 's), and with only silicon (blue O's). For the first case, the temperature difference was relatively lower than the latter two. With just ITO, the temperature difference as similar order of magnitude as that of ITO (10.2 W·m<sup>-1</sup>·K<sup>-1</sup> at room temperature [134]) did the temperature difference

become quite small. In that case, incident heat easily spread through the CNT forest perpendicularly as it did through the ITO. Lastly, with just silicon, although the temperature difference started off very high, it also dropped rapidly. These results reveal that the current device schematic was not optimal. Thermal contact with the silicon substrate and with the ITO electrodes has been shown to decrease the effective junction temperature difference.



Figure 54: Model 5 temperature along Z with (a) CNT, silicon, and ITO, (b) CNT and ITO, (c) CNT and Si under incident laser power of  $Q_0 = 283.5$  mW with varied  $\kappa_{CNT}$ , (d) temperature difference along Z as a function of  $\kappa_{CNT}$  for all three configurations

#### 5.5. Future Model Improvements

The simulations presented in this chapter have shown that it is possible to model the effects of inducing a photo-thermovoltage by laser irradiation on a forest of carbon nanotubes. However, as is the case with any model, assumptions and simplifications were made. The purpose of this subchapter is to shed some light on possible avenues for refinements and improvements to the existing models.

In the experimental measurement of conduction in the longitudinal conduction device, a heightadjustable stainless steel screw served as the voltage probe in contact with the top copper electrode. The screw was not included in the simulations as it was believed to be isothermal in experiments. Any voltage that would appear across the screw would therefore be negligible. As an addendum, the device geometry in Model 4 was further refined to study any potential heat-related effects of the stainless steel screw. A cylinder (diameter = 2 mm, length = 25 mm) with a 0.5 mm long cone (diameter = 1 mm at the tip) was placed in direct contact with the top surface of the top copper electrode. This body was given a surface-to-ambient radiation heat transfer boundary condition on all its exposed boundaries. Room temperature material properties of Type 304 stainless steel are as follows:  $\rho_d = 7900 \text{ kg} \cdot \text{m}^{-3}$  [84],  $c_p = 502 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$  [141],  $\kappa = 15 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$  [84],  $\varepsilon = 0.27$  [141].

Shown in parts (a) and (b) of Figure 55 below are the temperature difference and induced voltage difference as functions of incident laser power, respectively. The red X's represent the values from the bare device as before and the green  $\Box$ 's represent the values with the additional probing screw. The thermal conductivity of CNTs was not tuned, but was set to the curve that had been derived from Model 4. The screw effectively acted as a heat sink, decreased the temperature at the cold junction and, therefore, helped increase the temperature difference between the two junctions. There was as much as a 30% enhancement in the induced voltage, as shown in green  $\Box$ 's in part (b). However, in experiments, the screw was not flat and perfectly in contact with the top copper electrode, so there was most likely less of an enhancement in the induced voltage with the presence of the screw.

While most thermal systems simulated in COMSOL assume the use of thermal insulation on boundaries that do not radiate heat, in reality, devices are not free-floating and perfectly thermally insulated. The previous models could be further improved by considering the effects of the sample holders the devices were resting on. For example, in experiments, the longitudinal conduction device was resting on a slab of a thermally-insulative polymer, PEEK. The perpendicular conduction device was resting on a slab of Macor®, a high-temperature and vacuum-compatible ceramic insulator. Although both materials were insulators, they still have some thermal conductivity.

Considering the first device again, the cross-sectional area of the insulator was identical to that of the bottom copper electrode. As a test, a 2 mm thick slab of PEEK was added below the device in simulation just like it was in experiments. The exposed surfaces of the PEEK were given a surface-to-ambient radiation heat transfer boundary condition. The bottom surface, which was the surface in contact with the aluminum sample holder and the UHV chamber, was set to thermal insulation. Room temperature material properties of PEEK are as follows:  $\rho_d = 1320 \text{ kg} \cdot \text{m}^{-3}$ ,  $c_p = 1500 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ ,  $\kappa = 0.25 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ ,  $\varepsilon = 0.95$  [142]. Shown is blue O's in the same figure are the temperatures in part (a) and voltages in part (b) as functions of the same incident laser powers. Again, the thermal conductivity of CNTs was set to the curve derived from Model 4. With the presence of PEEK, in steady state, incident heat applied to the nanotubes was drawn into the bottom sufficient, the into the bottom copper, and finally into the PEEK. The temperature gradient across

the two copper contact electrodes was smaller than the bare device and, therefore, the voltages were as much as 70% smaller.

From here, a new CNT thermal conductivity curve will need to be derived based on these updated and potentially more realistic device schematics. Shown below in Figure 56 is a surface temperature plot on the left and a volume potential plot on the right of the device with both the attached screw and PEEK insulator. From the temperature plot, it is clear that the screw desirably draws away heat from the cold junction, but the insulator undesirably draws away some heat from the hot junction. A similar situation may be present in the perpendicular conduction device.



Figure 55: Model 4 (a) temperature difference and (b) induced voltage difference as functions of incident laser power with bare device (red X's), with screw probe (green  $\square$ 's), and with screw probe and PEEK support insulator (blue O's)



Figure 56: Model 4 (left) surface temperature and (right) volume potential plot under incident laser power of  $Q_0 = 405$  mW with screw probe and PEEK support insulator

However, the concept of thermal contact resistance has also been omitted from these simulations. Materials touching one another were modelled to be in perfect, direct contact with one another. In reality, materials have a surface roughness that can be on the order of nanometers to microns. This roughness puts many small gaps between the two materials. Heat flux is effectively reduced as the thermal resistance is increased. If, for example, the sample was in ambient air, there would be surface-to-surface radiation between the two materials trough the gap.

In COMSOL, thermal contact resistance can be modelled [122]. Constriction conductance using either the Cooper-Mikic-Yovanovich or the Mikic elastic correlation requires gap conductance as an input. The surface roughness average height and average slope must be inputted, alongside contact pressure and microhardness inputs. Considering that the surface roughness of the materials may be on a similar order of magnitude as the diameters of a bundle of MWCNTs, for example, thermal contact resistance can arguably be quite relevant and important when simulating CNT-based thermoelectric devices. Careful investigation of the thermal contact resistance parameters could be the focus of future work.

## 5.6. Summary

In this chapter, a computer model was described in which the two thermoelectric devices (longitudinal conduction and perpendicular conduction) were first drawn to scale in 3D. In the COMSOL Multiphysics software, the Heat Transfer module was coupled together with the AC/DC module to simulate the thermoelectric effect with temperature as a coupling variable. A 2D Gaussian heat flux profile was utilized to take into effect the focused laser beam's elliptical-shaped radial heat spread and subsequent exponential absorption into the respective materials at the hot junction.

For the longitudinal conduction device, the first and second models assumed room temperature material parameters derived from the literature and our experiments, respectively. The third model used experimentally-measured parameters, but with a tuned CNT thermal conductivity to match the simulated steady-state thermoelectric voltages with those measured in experiments. Lastly, the fourth model assumed temperature-dependent material parameters from a mixture of literature and our experiments. The CNT thermal conductivity was tuned in the same manner and it was seen to fall-off with increasing temperature.

For the perpendicular conduction device, the model was largely based on the method and results from the fourth model of the previous device. The predicted thermoelectric voltage matched very well with experimental results at the same setpoint laser powers. We can conclude that our model can accurately simulate thermoelectric energy generation induced by the irradiated heat from a laser beam. Steering the laser heat spot in simulation showed that movements in the *x* direction away from the middle of the sample junction result in symmetric decreases. In the *y* direction for both the longitudinal and perpendicular conduction devices, there existed an optimal position where the induced voltage can be maximized. A future work should pay more careful attention to the positioning of the laser beam if one wishes to maximize the induced thermoelectric voltage.

From these results, the room-temperature dimensionless figure-of-merit of our CNT forest in the longitudinal direction can be estimated from the following experimental results. If T = 300 K,  $\alpha = 16.5 \mu$ V·K<sup>-1</sup> (Chapter 3.3.2),  $\sigma = 352.2$  S·m<sup>-1</sup> (Chapter 3.4.1), and  $\kappa = 15$  W·m<sup>-1</sup>·K<sup>-1</sup> (approximate extrapolation from Chapter 5.3.4), *ZT* is therefore approximately **1.9x10<sup>-6</sup>** at room temperature. Similarly and in the perpendicular direction, if T = 300 K,  $\alpha = 8.0 \mu$ V·K<sup>-1</sup> (Chapter 3.3.2),  $\sigma = 97.1$  S·m<sup>-1</sup> (Chapter 3.4.1), and  $\kappa = 1.5$  W·m<sup>-1</sup>·K<sup>-1</sup> (approximate extrapolation from Chapter 5.3.4), *ZT* is approximate extrapolation from Chapter 5.3.4).

While the *ZT* of our carbon nanotubes certainly is not high or, in other words, they are not a very efficient thermoelectric material, we have performed no optimization towards the fabrication of the material or on the devices it was coupled with. Moreover, a low *ZT* does not necessarily imply a poor choice. Carbon nanotube forests certainly have the potential for use in thermoelectric energy generation if they are to be used in thermoelectric devices operated at higher temperatures where the Seebeck coefficient and electrical conductivity increase, the thermal conductivity decreases, and the *ZT* increases. If the perpendicular conduction directions are to be taken advantage of, *ZT* can be further enhanced. CNTs can also be a good choice of material if cost and low toxicity are concerns, since the CVD process is fairly inexpensive and carbon-containing precursors are widely abundant. As well as this, CNTs have a high power-to-weight ratio since carbon itself has a very low atomic mass and carbon nanotube forests are mostly empty space. Moreover, by enabling the unusual "Heat Trap" heating mechanism, they allow for higher temperature gradients to be maintained than regular bulk materials, under optical irradiation, which enables novel types of thermoelectric devices for the conversion of light to heat to electricity.

# Chapter 6 – Summary, Conclusion, and Future Work

Prior to this work, there have only been a handful of reports in the literature on the photo-thermoelectric effect in carbon nanotubes, i.e. the conversion of light to heat to electricity in the solid state. Most of the work has focussed on sheets or films of SWCNTs for UV, visible, or infrared photodetector applications. The research on the photo-thermoelectric effect in MWCNT forests has been limited to thermal diffusivity [51-53] and thermal conductivity [54] measurements. This thesis describes two novel photo-thermoelectric devices capable of producing a thermoelectric voltage by visible laser irradiation on aligned or forests of multi-walled carbon nanotubes, based on two intrinsic material properties described later in this chapter. A summary of the contributions of this work, as well as some suggestions for future studies, are presented here.

## 6.1. Contributions

The contributions of this thesis and their immediate applications are as follows:

- 1. Chapter 2 described the growth mechanism by which millimetre-long forests of multi-walled carbon nanotubes were grown by catalytic chemical vapour deposition. The growth apparatus and recipe was described, where the mass flow controllers were calibrated for improved growth accuracy. A custom LabVIEW program capable of systematically and automatically controlling the substrate growth temperature was presented. Optimization of the growth temperature revealed a specific temperature at which carbon nanotube forests grew the tallest. This technique and apparatus currently enables other students at UBC to pursue other applications, including thermionic electron emission from CNTs and the growth of graphene.
- 2. Chapter 3 described the theory and custom experimental apparatuses behind how the Seebeck coefficient and the electrical conductivity were measured. The temperature-dependence of the Seebeck coefficient of our CNT forests and their silicon substrates were independently measured in ambient conditions using copper contact electrodes, which showed a good agreement with published data in the literature. The coefficient of CNTs was also briefly studied as a function of oxygen desorption under vacuum and subsequent oxygen adsorption upon reintroduction to atmospheric conditions. The room temperature electrical conductivities of copper, silicon, and our CNT forests were also measured, which also showed excellent agreement with the literature. Information on the material properties of CNTs can be very useful when predicting the thermal and electrical behaviour of a designed thermoelectric device in simulations.

- 3. Chapter 4 presented two novel photo-thermoelectric devices, where visible laser irradiation heated the junction between the CNT forest and another electrode (copper and silicon, or indium tin oxide) while the other junction was kept cool under high-vacuum conditions. In the first device, electrical and thermal conduction were primarily in the longitudinal direction with respect to the CNT growth direction. Utilizing the "Heat Trap" effect, the localization of light-induced heat, we showed that an induced voltage could be sustained upon irradiation at higher laser powers. In the second device, electrical and thermal conductivity of CNTs meant a larger temperature gradient could be maintained in the second device, which had the effect of a larger induced voltage. The power conversion efficiency of the second device was measured to be in the 10<sup>-5</sup> % range.
- 4. Chapter 5 showed the results from a finite element analysis simulation study. The Heat Transfer in Solids and Electric Currents modules in the COMSOL Multiphysics software were coupled together to study the Seebeck effect. In order to be as close to experiment as possible, a 2D Gaussian profile was analytically modelled that approximated the focused beam shape, as well as the effects of the absorption and reflection coefficients of the materials the laser was incident upon. For the first device, four models were presented in order of increasing complexity and accuracy. In the fourth model, the temperature-dependent Seebeck coefficients, electrical conductivities, and thermal conductivities of all materials were inputted when available. By tuning the thermal conductivity of the CNTs at each incident laser power, the induced voltage from experiment was matched with that in simulation to within 0.5 μV of precision. The temperature-dependent thermal conductivity of CNTs was derived from this study, which was used as an input in a fifth model to study the thermal and electrical behaviour of the second device. Without tuning any parameters, the simulated induced voltage matched up with the experimental values to within 10% at the higher incident laser powers. Results from these simulation models can be used to accurately predict the behaviour of new thermoelectric or photo-thermoelectric devices based on MWCNT forests.

## 6.2. Conclusion and Future Work

The usefulness of a thermoelectric device is ultimately determined by the dimensionless figure-of-merit *ZT*. From a literature survey, the room temperature *ZT* value for CNTs has been measured for a wide range of morphologies. It has been measured to be in the  $10^{-5}$  range for MWCNT pellets [88], in the  $10^{-4}$  range for SWCNT bundles [143], films [102], and MWCNT forests [87], and as high as  $10^{-3}$  for DWCNT bundles [24], MWCNT powders [14], CNT sheets or papers [16, 25], or composites with polymers [26-28]. All of these results are in fact quite small compared to commercially well-established thermoelectric materials that have a *ZT* greater than 1. However, this should not disprove the usefulness of carbon nanotubes for

thermoelectric applications. CNTs can be a good choice of material if low cost and low toxicity are concerns, since the CVD process is fairly inexpensive and carbon-containing precursors are abundant. As well as this, CNTs have a high power-to-weight ratio since carbon has a very low atomic mass and carbon nanotube forests are mostly empty space.

Although the room temperature *ZT* measured in this work (10<sup>-6</sup> range) was smaller compared to the literature, we note that no optimization was performed on nanotube growth aside from the growth temperature. This prompts future experiments on the effects of the annealing temperature and duration, the carrier and carbon-containing precursor gas ratios, and perhaps the downstream gas pressures. Water-assisted CVD, low-pressure CVD, and plasma-enhanced CVD could also be investigated, which may show improvements or optimizations in the forest height, density, alignment, or purity, to name a few. The chirality and number of nanotube walls can also be tuned. Depending on the chirality of a CNT, a single-walled CNT can exhibit a mixture of metallic and semiconducting properties; semiconductors typically have Seebeck coefficients an order of magnitude larger than metals. Through doping, B-doped and N-doped MWCNTs have shown simultaneous increases in the Seebeck coefficient and decreases in the thermal conductivity, leading to large increases in the figure-of-merit [88]. After the CVD process, forests of nanotubes can be further purified or densified through chemical means, which could result in further enhancements to their thermoelectric properties. As well, composites with other materials could be used. For example, a nanocomposite of CNTs and polyaniline (a conducting polymer) has shown improved Seebeck coefficients and electrical conductivities [28, 144] compared to the individual materials.

If one desires to maximize the power conversion efficiency, CNT-based thermoelectric or photothermoelectric devices can be operated at elevated temperatures, where the CNT Seebeck coefficient and electrical conductivity increases, thermal conductivity decreases, and therefore ZT increases. If the perpendicular conduction directions are to be taken advantage of, the temperature gradient and ZT can be further enhanced due to a smaller CNT thermal conductivity in this direction.

CNTs exhibit the unusual "Heat Trap" heating mechanism under optical irradiation, allowing for higher temperature gradients to be maintained compared with regular bulk materials. Although performed with a single wavelength in this work, the effect of the laser wavelength and polarization could reveal interesting phenomena that are not immediately apparent. The photo-thermoelectric effect in MWCNT forests thus enables novel types of devices to detect light and harness electricity from light sources, whether it be from a laser source, from collected and focused waste light, or from the sun as in remote or space applications.

# References

- [1] U. S. Department of Energy, "Waste Heat Recovery: Technology and Opportunities in U.S. Industry," BCS Incorporated, 2008.
- [2] R. C. O'Brien, R. M. Ambrosia, N. P. Bannistera, S. D. Howeb, and H. V. Atkinson, "Safe radioisotope thermoelectric generators and heat sources for space applications," *Journal of Nuclear Materials*, vol. 377, no. 3, pp. 506-521, 2008.
- [3] A. H. Khoshaman, H. D. E. Fan, A. T. Koch, G. A. Sawatzky, and A. Nojeh, "Thermionics, Thermoelectrics, and Nanotechnology - New possibilities for old ideas," *IEEE Nanotechnology Magazine*, vol. 8, no. 2, pp. 4-15, 2014.
- [4] H. J. goldsmid, Introduction to Thermoelectricity, Berlin Heidelberg: Springer-Verlag, 2010.
- [5] K. A. Chao, and M. Larsson, "Thermoelectric Phenomena from Macro-Systems to Nano-Systems," *Physics of Zero- and One-Dimensional Nanoscopic Systems*, pp. 151-186: Springer, 2007.
- [6] D. M. Rowe, *Thermoelectrics Handbook Macro to Nano*, Boca Raton, FL: Taylor & Francis Group, 2006.
- [7] B. Bhushan, "12. Nanometer-Scale Thermoelectric Materials," *Springer Handbook of Nanotechnology*, pp. 345-373: Springer, 2007.
- [8] A. F. Ioffe, *Semiconductor Thermoelements and Thermoelectric Cooling*, London: Infosearch Ltd., 1957.
- [9] T. M. Tritt, and M. A. Subramanian, "Thermoelectric materials, phenomena, and applications: A bird's eye view," *MRS Bulletin*, vol. 31, no. 3, pp. 188-194, 2006.
- [10] P. Pichanusakorn, and P. Bandaru, "Nanostructured thermoelectrics," *Materials Science and Engineering R*, vol. 67, no. 2-4, pp. 19-63, 2010.
- [11] T. C. Harman, P. J. Taylor, M. P. Walsh, and B. E. LaForge, "Quantum Dot Superlattice Thermoelectric Materials and Devices," *Science*, vol. 297, no. 5590, pp. 2229-2232, 2002.
- [12] R. Venkatasubramanian, E. Siivola, T. Colpitts, and B. O'Quinn, "Thin-film thermoelectric devices with high room-temperature figures of merit," *Nature*, vol. 413, no. 6856, pp. 597-602, 2001.
- [13] L.-D. Zhao, S.-H. Lo, Y. Zhang, H. Sun, G. Tan, C. Uher, C. Wolverton, V. P. Dravid, and M. G. Kanatzidis, "Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals," *Nature*, vol. 508, no. 7496, pp. 373-377, 2014.
- [14] H.-L. Zhang, J.-F. Li, B.-P. Zhang, K.-F. Yao, W.-S. Liu, and H. Wang, "Electrical and thermal properties of carbon nanotube bulk materials: Experimental studies for the 328-958 K temperature range," *Physical Review B*, vol. 75, no. 20, pp. 205407-1 - 205407-9, 2007.
- [15] S. Jung, K.-B. Kim, G. Fernandes, J. H. Kim, F. Wahab, and J. Xu, "Enhanced thermoelectric power in nanopatterned carbon nanotube film," *Nanotechnology*, vol. 23, no. 13, pp. 135704-1 -135704-4, 2012.
- [16] W. Zhao, S. Fan, N. Xiao, D. Liu, Y. Y. Tay, C. Yu, D. Sim, H. H. Hng, Q. Zhang, F. Boey, J. Ma, X. Zhao, H. Zhang, and Q. Yan, "Flexible carbon nanotube papers with improved thermoelectric properties," *Energy & Environmental Science*, vol. 5, no. 1, pp. 5364-5369, 2012.
- [17] Y.-B. Gao, Y. Wang, J.-Y. Wang, S.-Y. Xu, X.-L. Wei, M.-S. Wang, Y. Li, and L.-M. Peng, "Thermoelectric Measurement of Multi-Walled Carbon Nanotube Bundles by Using Nano-Probes," *Journal of Nanoscience and Nanotechnology*, vol. 10, no. 8, pp. 4985-4991, 2010.
- [18] W. Zhang, Z. Zhu, F. Wang, T. Wang, L. Sun, and Z. Wang, "Chirality dependence of the thermal conductivity of carbon nanotubes," *Nanotechnology*, vol. 15, no. 8, pp. 936-939, 2004.
- [19] G. Zhang, and B. Li, "Thermal conductivity of nanotubes revisited: Effects of chirality, isotope impurity, tube length, and temperature," *The Journal of Chemical Physics*, vol. 123, no. 11, pp. 114714-1-4, 2005.

- [20] X. Tan, H. Liu, Y. Wen, H. Lv, L. Pan, J. Shi, and X. Tang, "Optimizing the thermoelectric performance of zigzag and chiral carbon nanotubes," *Nanoscale Research Letters* vol. 7, no. 116, pp. 1-7, 2012.
- [21] S. Maruyama, "A molecular dynamics simulation of heat conduction of a finite length singlewalled carbon nanotube," *Microscale Thermophysical Engineering*, vol. 7, no. 1, pp. 41-50, 2003.
- [22] A. V. Savin, B. Hu, and Y. S. Kivshar, "Thermal conductivity of single-walled carbon nanotubes," *Physical Review B*, vol. 80, no. 19, pp. 195423-1-20, 2009.
- [23] M. Akoshima, K. Hata, D. N. Futaba, K. Mizuno, T. Baba, and M. Yumura, "Thermal Diffusivity of Single-Walled Carbon Nanotube Forest Measured by Laser Flash Method," *Japanese Journal* of Applied Physics, vol. 48, no. 5, pp. 05EC07-1-6, 2009.
- [24] T. Miao, W. Ma, X. Zhang, J. Wei, and J. Sun, "Significantly enhanced thermoelectric properties of ultralong double-walled carbon nanotube bundle," *Applied Physics Letters*, vol. 102, no. 5, pp. 053105-1-5, 2013.
- [25] C. Hu, C. Liu, L. Chen, C. Meng, and S. Fan, "A Demo Opto-electronic Power Source Based on Single-Walled Carbon Nanotube Sheets," ACS Nano, vol. 4, no. 8, pp. 4701-4706, 2010/08/24, 2010.
- [26] Q. Yao, L. Chen, W. Zhang, S. Liufu, and X. Chen, "Enhanced Thermoelectric Performance of Single-Walled Carbon Nanotubes/Polyaniline Hybrid Nanocomposites," ACS Nano, vol. 4, no. 4, pp. 2445-2451, 2010.
- [27] C. Yu, Y. S. Kim, D. Kim, and J. C. Grunlan, "Thermoelectric Behavior of Segregated-Network Polymer Nanocomposites," *Nano Letters*, vol. 8, no. 12, pp. 4428-4432, 2008/12/10, 2008.
- [28] Z. Kun, D. Marauo, Q. Jingjing, H.-W. Louisa, and W. Shiren, "Thermoelectric properties of porous multi-walled carbon nanotube/polyaniline core/shell nanocomposites," *Nanotechnology*, vol. 23, no. 38, pp. 385701, 2012.
- [29] K. Mizuno, J. Ishii, H. Kishida, Y. Hayamizu, S. Yasuda, D. N. Futaba, M. Yumura, and K. Hata, "A black body absorber from vertically aligned single-walled carbon nanotubes," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 106, no. 15, pp. 6044-6047, 2009.
- [30] P. Yaghoobi, M. V. Modhaddam, and A. Nojeh, ""Heat trap": Light-induced localized heating and thermionic electron emission from carbon nanotube arrays," *Solid State Communications*, vol. 151, no. 17, pp. 1105-1108, 2011.
- [31] M. A. Osman, and D. Srivastava, "Temperature dependence of the thermal conductivity of singlewall carbon nanotubes," *Nanotechnology*, vol. 12, no. 1, pp. 21-24, 2001.
- [32] N. Kondo, T. Yamamoto, and K. Watanabe, "Molecular-dynamics simulations of thermal transport in carbon nanotubes with structural defects," *e-Journal of Surface Science and Nanotechnology 17 February*, vol. 4, pp. 239-243, 2006.
- [33] J. Che, T. Çağın, and W. A. Goddard III, "Thermal conductivity of carbon nanotubes," *Nanotechnology*, vol. 11, no. 2, pp. 65-69, 2000.
- [34] E. Pop, D. Mann, J. Cao, Q. Wang, K. Goodson, and H. Dai, "Negative Differential Conductance and Hot Phonons in Suspended Nanotube Molecular Wires," *Physical Review Letters*, vol. 95, no. 15, pp. 155505-1, 2005.
- [35] E. Pop, D. A. Mann, K. E. Goodson, and H. Dai, "Electrical and thermal transport in metallic single-wall carbon nanotubes on insulating substrates," *Journal of Applied Physics*, vol. 101, no. 9, pp. 093710-1-10, 2007.
- [36] E. Pop, D. Mann, Q. Wang, K. Goodson, and H. Dai, "Thermal Conductance of an Individual Single-Wall Carbon Nanotube above Room Temperature," *Nano Letters*, vol. 6, no. 1, pp. 96-100, 2006.
- [37] M. Chang, M. V. Moghaddam, A. Khoshaman, M. Dahmardeh, K. Takahata, and A. Nojeh, "High temperature gradient in a conductor: Carbon nanotube forest under the "Heat Trap" condition," *Proceedings of the 57th International Conference on Electron, Ion, and Photon Beam Technology and Nanofabrication (EIPBN '13)*, 2013.

- [38] L. Ji, W. He, L. Hu, Z. Liu, H. Zhou, X. Wu, and S. Lianfeng, "Visible light detection using single-walled carbon nanotube film and gold nanoparticles or nanorods," *Journal of Applied Physics*, vol. 107, no. 9, pp. 094311-094311-3, 2010.
- [39] S. Nanot, A. W. Cummings, C. L. Pint, A. Ikeuchi, T. Akiho, K. Sueoka, R. H. Hauge, F. Léonard, and J. Kono, "Broadband, Polarization-Sensitive Photodetector Based on Optically-Thick Films of Macroscopically Long, Dense, and Aligned Carbon Nanotubes," *Scientific Reports*, vol. 3, 02/27/online, 2013.
- [40] M. Omari, and N. A. Kouklin, "Photothermovoltaic effect in carbon nanotubes: En route toward junctionless infrared photocells and light sensors," *Applied Physics Letters*, vol. 98, no. 24, pp. 243113, 2011.
- [41] X. He, X. Wang, S. Nanot, K. Cong, Q. Jiang, A. A. Kane, J. E. M. Goldsmith, R. H. Hauge, F. Léonard, and J. Kono, "Photothermoelectric p–n Junction Photodetector with Intrinsic Broadband Polarimetry Based on Macroscopic Carbon Nanotube Films," ACS Nano, vol. 7, no. 8, pp. 7271-7277, 2013/08/27, 2013.
- [42] B. C. St-Antoine, D. Ménard, and R. Martel, "Single-Walled Carbon Nanotube Thermopile For Broadband Light Detection," *Nano Letters*, vol. 11, no. 2, pp. 609-613, 2011/02/09, 2010.
- [43] T. DeBorde, L. Aspitarte, T. Sharf, J. W. Kevek, and E. D. Minot, "Photothermoelectric Effect in Suspended Semiconducting Carbon Nanotubes," ACS Nano, vol. 8, no. 1, pp. 216-221, 2014/01/28, 2013.
- [44] M. Kuriakose, M. Depriester, R. Chan Yu King, F. Roussel, and A. Hadj Sahraoui, "Photothermoelectric effect as a means for thermal characterization of nanocomposites based on intrinsically conducting polymers and carbon nanotubes," *Journal of Applied Physics*, vol. 113, no. 4, pp. 044502, 2013.
- [45] M. Kuriakose, M. Depriester, R. King, F. Roussel, and A. Sahraoui, "Use of Photothermally Generated Seebeck Voltage for Thermal Characterization of Thermoelectric Materials," *Journal* of *Electronic Materials*, vol. 43, no. 6, pp. 1740-1743, 2014/06/01, 2014.
- [46] B. C. St-Antoine, D. Ménard, and R. Martel, "Position Sensitive Photothermoelectric Effect in Suspended Single-Walled Carbon Nanotube Films," *Nano Letters*, vol. 9, no. 10, pp. 3503-3508, 2009.
- [47] S. Wang, Z. Bai, G. Yan, H. Zhang, J. Wang, W. Yu, and G. Fu, "The enhancement of photothermo-electric conversion in tilted Bi2Sr2Co2Oy thin films through coating a layer of singlewall carbon nanotubes light absorber," *Optics Express*, vol. 21, no. 15, pp. 18336-18343, 2013.
- [48] B. St-Antoine, D. Ménard, and R. Martel, "Photothermoelectric effects in single-walled carbon nanotube films: Reinterpreting scanning photocurrent experiments," *Nano Research*, vol. 5, no. 2, pp. 73-81, 2012/02/01, 2012.
- [49] E. Miyako, H. Nagata, R. Funahashi, K. Hirano, and T. Hirotsu, "Light-Triggered Thermoelectric Conversion Based on a Carbon Nanotube–Polymer Hybrid Gel," *ChemSusChem*, vol. 2, no. 5, pp. 419-422, 2009.
- [50] E. Miyako, H. Nagata, R. Funahashi, K. Hirano, and T. Hirotsu, "Light-Driven Thermoelectric Conversion Based on a Carbon Nanotube–Ionic Liquid Gel Composite," *ChemSusChem*, vol. 2, no. 8, pp. 740-742, 2009.
- [51] T. Borca-Tasciuc, D. A. Borca-Tasciuc, and G. Chen, "A photo-thermoelectric technique for anisotropic thermal diffusivity characterization of nanowire/nanotube composites," *Twenty First Annual IEEE Semiconductor Thermal Measurement and Management Symposium*, pp. 283-291, 15-17 March 2005, 2005.
- [52] T. Borca-Tasciuc, S. Vafaei, D.-A. Borca-Tasciuc, B. Q. Wei, R. Vajtai, and P. M. Ajayan, "Anisotropic thermal diffusivity of aligned multiwall carbon nanotube arrays," *Journal of Applied Physics*, vol. 98, no. 5, pp. 054309, 2005.
- [53] T. Borca-Tasciuc, D. A. Borca-Tasciuc, and G. Chen, "Photo-Thermoelectric Technique for Anisotropic Thermal Diffusivity Measurements," *IEEE Transactions on Components and Packaging Technologies*, vol. 30, no. 4, pp. 609-617, 2007.

- [54] Y. Son, "Study of anisotropic thermal properties and thermal transport at the interface in nanostructured materials," Mechanical Engineering, Rensselaer Polytechnic Institute, 2008.
- [55] M. Kumar, and Y. Ando, "Chemical Vapor Deposition of Carbon Nanotubes: A Review on Growth Mechanism and Mass Production," *Journal of Nanoscience and Nanotechnology*, vol. 10, no. 6, pp. 3739-3758, 2010.
- [56] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tománek, J. E. Fischer, and R. E. Smalley, "Crystalline Ropes of Metallic Carbon Nanotubes," *Science*, vol. 273, no. 5274, pp. 483-487, 1996.
- [57] A. A. Gorbunov, A. Graff, O. Jost, and W. Pompe, "Mechanism of carbon nanotube synthesis by laser ablation," *Proceedings of SPIE The International Society for Optical Engineering*, vol. 4423, pp. 212-217, 2001.
- [58] S. B. Sinnott, R. Andrews, D. Qian, A. M. Rao, Z. Mao, E. C. Dickey, and F. Derbyshire, "Model of carbon nanotube growth through chemical vapor deposition," *Chemical Physics Letters*, vol. 315, no. 1–2, pp. 25-30, 1999.
- [59] R. Andrews, D. Jacques, A. M. Rao, F. Derbyshire, D. Qian, X. Fan, E. C. Dickey, and J. Chen, "Continuous production of aligned carbon nanotubes: a step closer to commercial realization," *Chemical Physics Letters*, vol. 303, no. 5–6, pp. 467-474, 1999.
- [60] A. Gohier, C. P. Ewels, T. M. Minea, and M. A. Djouadi, "Carbon nanotube growth mechanism switches from tip- to base-growth with decreasing catalyst particle size," *Carbon*, vol. 46, no. 10, pp. 1331-1338, 2008.
- [61] D. N. Futaba, K. Hata, T. Namai, T. Yamada, K. Mizuno, Y. Hayamizu, M. Yumura, and S. Iijima, "84% Catalyst Activity of Water-Assisted Growth of Single Walled Carbon Nanotube Forest Characterization by a Statistical and Macroscopic Approach," *Journal of Physical Chemistry B*, vol. 110, no. 15, pp. 8035-8038, 2006.
- [62] Z. Liu, L. Ci, S. Kar, P. M. Ajayan, and J.-Q. Lu, "Fabrication and Electrical Characterization of Densified Carbon Nanotube Micropillars for IC Interconnection," *IEEE Transactions on Nanotechnology*, vol. 8, no. 2, pp. 196-203, 2009.
- [63] O. A. Louchev, Y. Sato, and H. Kanda, "Growth mechanism of carbon nanotube forests by chemical vapor deposition," *Applied Physics Letters*, vol. 80, no. 15, pp. 2752-2754, 2002.
- [64] A.-C. Dupuis, "The catalyst in the CCVD of carbon nanotubes—a review," *Progress in Materials Science*, vol. 50, no. 8, pp. 929-961, 2005.
- [65] F. Ding, P. Larsson, J. A. Larsson, R. Ahuja, H. Duan, A. Rosén, and K. Bolton, "The Importance of Strong Carbon–Metal Adhesion for Catalytic Nucleation of Single-Walled Carbon Nanotubes," *Nano Letters*, vol. 8, no. 2, pp. 463-468, 2007.
- [66] Y. Li, W. Kim, Y. Zhang, M. Rolandi, D. Wang, and H. Dai, "Growth of Single-Walled Carbon Nanotubes from Discrete Catalytic Nanoparticles of Various Sizes," *The Journal of Physical Chemistry B*, vol. 105, no. 46, pp. 11424-11431, 2001.
- [67] C. L. Cheung, A. Kurtz, H. Park, and C. M. Lieber, "Diameter-Controlled Synthesis of Carbon Nanotubes," *The Journal of Physical Chemistry B*, vol. 106, no. 10, pp. 2429-2433, 2002.
- [68] C. Zhang, S. Pisana, C. T. Wirth, A. Parvez, C. Ducati, S. Hoffman, and J. Robertson, "Growth of aligned millimeter-long carbon nanotube by chemical vapor deposition," *Diamond and Related Materials*, vol. 17, no. 7-10, pp. 1447-1451, 2008.
- [69] P. Yaghoobi, "Laser-Induced Electron Emission from Arrays of Carbon Nanotubes," Electrical and Computer Engineering, The University of British Columbia, 2012.
- [70] A. J. Hart, L. van Laake, and A. H. Slocum, "Desktop Growth of Carbon-Nanotube Monoliths with In Situ Optical Imaging," *Small*, vol. 3, no. 5, pp. 772-777, 2007.
- [71] J. Wu, Q. Huang, Y. Ma, Y. Huang, Z. Liu, X. Yang, Y. Chen, and D. Chen, "Distortion of carbon nanotube array and its influence on carbon nanotube growth and termination," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 313-314, no. 1, pp. 13-17, 2008.

- [72] L. Delzeit, C. V. Nguyen, B. Chen, R. Stevens, A. Cassell, J. Han, and M. Meyyappan, "Multiwalled Carbon Nanotubes by Chemical Vapor Deposition Using Multilayered Metal Catalysts," *Journal of Physical Chemistry B* vol. 106, no. 22, pp. 5629-5635, 2002.
- [73] A. J. Hart, and A. H. Slocum, "Rapid Growth and Flow-Mediated Nucleation of Millimeter-Scale Aligned Carbon Nanotube Structures from a Thin-Film Catalyst," *Journal of Physical Chemistry B*, vol. 110, no. 16, pp. 8250-8257, 2006.
- [74] S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Cassel, and H. Dai, "Self-Oriented Regular Arrays of Carbon Nanotubes and Their Field Emission Properties," *Science, New Series*, vol. 283, no. 5401, pp. 512-514, 1999.
- [75] L. van Laake, A. J. Hart, and A. H. Slocum, "Suspended heated silicon platform for rapid thermal control of surface reactions with application to carbon nanotube synthesis," *Review of Scientific Instrument*, vol. 78, no. 8, pp. 015104-1-9, 2007.
- [76] G. D. Nessim, A. J. Hart, J. S. Kim, D. Acquaviva, J. Oh, C. Morgan, M. Seita, J. S. Leib, and C. V. Thompson, "Tuning of Vertically-Aligned Carbon Nanotube Diameter and Areal Density through Catalyst Pre-Treatment," *Nano Letters*, vol. 8, no. 11, pp. 3587-3593, 2008.
- [77] W. Chiang, D. N. Futaba, M. Yumura, and K. Hata, "Growth control of single-walled, doublewalled, and triple-walled carbon nanotube forests by a priori electrical resistance measurement of catalyst films," *Carbon*, vol. 49, no. 13, pp. 4368-4375, 2011.
- [78] S. Chakrabarti, T. Nakasaka, Y. Yoshikawa, L. Pan, and Y. Nakayama, "Growth of super long aligned brush-like carbon nanotubes," *Japanese Journal of Applied Physics*, vol. 45, no. 28, pp. L720-L722, 2006.
- [79] G. D. Nessim, A. Al-Obeidi, H. Grisaru, E. S. Polsen, C. R. Oliver, T. Zimrin, A. J. Hart, D. Aurbach, and C. V. Thompson, "Synthesis of tall carpets of vertically aligned carbon nanotubes by in situ generation of water vapor through preheating of added oxygen," *Carbon*, vol. 50, no. 11, pp. 4002-4009, 2012.
- [80] H. Nishino, S. Yasuda, T. Namai, D. N. Futaba, T. Yamada, M. Yumura, S. Iijima, and K. Hata, "Water-Assisted Highly Efficient Synthesis of Single-Walled Carbon Nanotubes Forests from Colloidal Nanoparticle Catalysts," *Journal of Physical Chemistry C*, vol. 111, no. 48, pp. 17961-1796, 2007.
- [81] M. G. Kanatzidis, S. D. Mahanti, and T. P. H. (eds.), Chemistry, Physics, and Materials Science of Thermoelectric Materials: Beyond Bismuth Telluride, 1st ed.: Springer-Science+Business Media, LLC, 2003.
- [82] N. Cusack, and P. Kendall, "The Absolute Scale of Thermoelectric Power at High Temperature," *Proceedings of the Physical Society*, vol. 72, no. 5, pp. 898-901, 1958.
- [83] G. Wypych, "Handbook of Polymers," ChemTec Publishing, 2012.
- [84] CRC Handbook of Chemistry and Physics, Boca Raton, FL: CRC Press, 2014.
- [85] M. B. Jakubinek, M. A. White, G. Li, C. Jayasinghe, W. Cho, M. J. Schulz, and V. Shanov, "Thermal and electrical conductivity of tall, vertically aligned carbon nanotube arrays," *Carbon*, vol. 48, no. 13, pp. 3947-3952, 2010.
- [86] W. Fulkerson, J. P. Moore, R. K. Williams, R. S. Graves, and D. L. McElroy, "Thermal Conductivity, Electrical Resistivity, and Seebeck Coefficient of Silicon from 100 to 1300°K," *Physical Review*, vol. 167, no. 3, pp. 765-782, 1968.
- [87] J. Chen, X. Gui, Z. Wang, Z. Li, R. Xiang, K. Wang, D. Wu, X. Xia, Y. Zhou, Q. Wang, Z. Tang, and L. Chen, "Superlow thermal conductivity 3D carbon nanotube network for thermoelectric applications," *ACS Applied Materials & Interfaces*, vol. 4, no. 1, pp. 81-86, 2012.
- [88] I. Kunadian, R. Andrews, M. P. Mengüç, and D. Qian, "Thermoelectric power generation using doped MWCNTs," *Carbon*, vol. 47, no. 3, pp. 589-601, 2009.
- [89] R. Jin, Z. X. Zhou, D. Mandrus, I. N. Ivanov, G. Eres, J. Y. Howe, A. A. Puretzky, and D. B. Geohegan, "The effect of annealing on the electrical and thermal transport properties of macroscopic bundles of long multi-wall carbon nanotubes," *Physica B: Condensed Matter*, vol. 388, no. 1-2, pp. 326-320, 2007.
- [90] M. Penza, R. Rossi, M. Alvisi, D. Valerini, E. Serra, E. Martinelli, C. Di Natale, and A. D'amico, "Thermoelectric Properties of Carbon Nanotubes Layers," *Sensors and Microsystems - AISEM* 2010 Proceedings, vol. 91, pp. 73-70, 2011.
- [91] K. Yang, J. He, Z. Su, J. B. Reppert, M. J. Skove, T. M. Tritt, and A. M. Rao, "Inter-tube bonding, graphene formation and anisotropic transport properties in spark plasma sintered multi-wall carbon nanotube arrays," *Carbon*, vol. 48, no. 3, pp. 756-762, 2010.
- [92] P. G. Collins, K. Bradley, M. Ishigami, and A. Zettl, "Extreme Oxygen Sensitivity of Electronic Properties of Carbon Nanotubes," *Science*, vol. 287, no. 5459, pp. 1801-1804, 2000.
- [93] G. U. Sumanasekera, C. K. W. Adu, S. Fang, and P. C. Eklund, "Effects of Gas Adsorption and Collisions on Electrical Transport in Single-Walled Carbon Nanotubes," *Physical Review Letters*, vol. 85, no. 5, pp. 1096-1099, 2000.
- [94] G. U. Sumanasekera, B. K. Pradhan, C. K. W. Adu, H. E. Romero, H. C. Foley, and P. C. Eklund, "Thermoelectric chemical sensor based on single wall carbon nanotubes," *Molecular Crystals* and Liquid Crystals, vol. 387, no. 1, pp. 31-37, 2002.
- [95] K. McGuire, N. Gothard, P. L. Gai, M. S. Dresselhaus, G. Sumanasekera, and A. M. Rao, "Synthesis and Raman characterization of boron-doped single-walled carbon nanotubes," *Carbon*, vol. 43, no. 2, pp. 219-227, //, 2005.
- [96] C. Qin, X. Shi, S. Q. Bai, L. D. Chen, and L. J. Wang, "High temperature electrical and thermal properties of the bulk carbon nanotube prepared by SPS," *Materials Science and Engineering A*, vol. 420, no. 1-2, pp. 208-211, 2006.
- [97] T. Savage, S. Bhattacharya, B. Sadanadan, J. Gaillard, T. M. Tritt, Y. P. Sun, Y. Wu, S. Nayak, R. Car, N. Marzari, P. M. Ajayan, and A. M. Rao, "Photoinduced oxidation of carbon nanotubes," *Journal of Physics: Condensed Matter*, vol. 15, no. 35, pp. 5915, 2003.
- [98] H. Topsøe, Geometric factors in four point resistivity measurement, Bridge Technology, 1968.
- [99] PVLighthouse. "Resistivity Calculator," http://www.pvlighthouse.com.au/calculators/Resistivity%20calculator/Resistivity%20calculator.a spx.
- [100] D. B. M. Klaassen, "A unified mobility model for device simulation—I. Model equations and concentration dependence," *Solid-State Electronics*, vol. 35, no. 7, pp. 953-959, 1992.
- [101] D. B. M. Klaassen, "A unified mobility model for device simulation—II. Temperature dependence of carrier mobility and lifetime," *Solid-State Electronics*, vol. 35, no. 7, pp. 961-967, 1992.
- [102] G. E. Fernandes, J. H. Kim, and J. Xu, "Thermoelectric response of carbon nanotube films to Aunanoparticle incorporation," *Materials Research Bulletin*, vol. 48, no. 8, pp. 2950-2954, 2013.
- [103] X. Huang, J. Wang, G. Eres, and X. Wang, "Thermophysical properties of multi-wall carbon nanotube bundles at elevated temperatures up to 830 K," *Carbon*, vol. 49, no. 5, pp. 1680-1691, 2011.
- [104] W. Lin, R. V. Olivares, Q. Liang, R. Zhang, K.-S. Moon, and C. P. Wong, "Vertically Aligned Carbon Nanotubes on Copper Substrates for Applications as Thermal Interface Materials: from Synthesis to Assembly," 9th IEEE Conference on Nanotechnology, 2009.
- [105] B. Zhao, D. N. Futaba, S. Yasuda, M. Akoshima, T. Yamada, and K. Hata, "Exploring Advantages of Diverse Carbon Nanotube Forests with Tailored Structures Synthesized by Supergrowth from Engineered Catalysts," *ACS Nano*, vol. 3, no. 1, pp. 108-114, 2009.
- [106] Y. Xie, "Solution-based Synthesis and Processing of Nanocrystalline ZrB2-based Composites," School of Materials Science and Engineering, Georgia Institute of Technology, 2008.
- [107] I. Ivanov, A. Puretzky, G. Eres, H. Wang, Z. Pan, H. Cui, R. Jin, J. Y. Howe, and D. B. Geohegan, "Fast and highly anisotropic thermal transport through vertically aligned carbon nanotube arrays," *Applied Physics Letters*, vol. 89, no. 22, pp. -, 2006.
- [108] S. Shaikh, L. Li, K. Lafdi, and J. Huie, "Thermal conductivity of an aligned carbon nanotube array," *Carbon*, vol. 45, no. 13, pp. 2608-2613, 2007.

- [109] D. J. Yang, Q. Zhang, G. Chen, S. F. Yoon, J. Ahn, S. G. Wang, Q. Zhou, Q. Wang, and J. Q. Li, "Thermal conductivity of multiwalled carbon nanotubes," *Physical Review B*, vol. 66, no. 16, pp. 165440, 2002.
- [110] H. Xie, A. Cai, and X. Wang, "Thermal diffusivity and conductivity of multiwalled carbon nanotube arrays," *Physics Letters A*, vol. 369, no. 1–2, pp. 120-123, 2007.
- [111] T. Tao, Z. Yang, L. Delzeit, A. Kashani, M. Meyyappan, and A. Majumdar, "Dense Vertically Aligned Multiwalled Carbon Nanotube Arrays as Thermal Interface Materials," *Components and Packaging Technologies, IEEE Transactions on*, vol. 30, no. 1, pp. 92-100, 2007.
- [112] J. R. Lukes, and H. Zhong, "Thermal Conductivity of Individual Single-Wall Carbon Nanotubes," *Journal of Heat Transfer*, vol. 129, no. 6, pp. 705-716, 2006.
- [113] M. S. Dresselhaus, and P. C. Eklund, "Phonons in carbon nanotubes," *Advances in Physics*, vol. 49, no. 6, pp. 705-814, 2000.
- [114] ThorLabs. "N-BK7 Laser Windows," Oct 21, 2014; http://www.thorlabs.com/newgrouppage9.cfm?objectgroup\_id=1121.
- [115] I. Coherent. "Verdi V2, V5 & V6," 1/26/15, 2015; http://www.coherent.com/downloads/VerdiV2V5V6\_DS\_final.pdf.
- [116] J. D. Majumdar, and I. M. (Eds.), *Laser-Assisted Fabrication of Materials*: Springer-Verlag Berlin Heidelberg, 2013.
- [117] Q.-L. Chen, K.-H. Xue, W. Shen, F.-F. Tao, S.-Y. Yin, and W. Xu, "Fabrication and electrochemical properties of carbon nanotube array electrode for supercapacitors," *Electrochimica Acta*, vol. 49, no. 24, pp. 4157-4161, 2004.
- [118] L. Gao, A. Peng, Z. Y. Wang, H. Zhang, Z. Shi, Z. Gu, G. Cao, and B. Ding, "Growth of aligned carbon nanotube arrays on metallic substrate and its application to supercapacitors," *Solid State Communications*, vol. 146, no. 9–10, pp. 380-383, 2008.
- [119] H. Zhang, G. Cao, Z. Wang, Y. Yang, Z. Shi, and Z. Gu, "Growth of manganese oxide nanoflowers on vertically-aligned carbon nanotube arrays for high-rate electrochemical capacitive energy storage," *Nano Lett*, vol. 8, no. 9, pp. 2664-8, 2008.
- [120] EdmundOptics. "1" x 1", ITO Coated EMI Shielded Plastic Window," Oct 23, 2014; http://www.edmundoptics.com/optics/windows-diffusers/visible-windows/ito-coated-emishielded-plastic-windows/83742.
- [121] COMSOL. "COMSOL Multiphysics®," 01/05/15, 2015; http://www.comsol.com/comsolmultiphysics.
- [122] COMSOL, Heat Transfer Module User's Guide Version 5.0, 2014.
- [123] COMSOL, AC/DC Moudle User's Guide Version 5.0, 2014.
- [124] S. T. Yang, M. J. Matthews, S. Elhadj, D. Cooke, G. M. Guss, V. G. Draggoo, and P. J. Wegner, "Comparing the use of mid-infrared versus far-infrared lasers for mitigating damage growth on fused silica," *Applied Optics*, vol. 49, no. 14, pp. 2606-2616, 2010.
- [125] COMSOL. "Model Gallery Laser Heating A Self Guided Tutorial, Model ID: 12317," 1/23/15, 2015; http://www.comsol.com/model/laser-heating-a-self-guided-tutorial-12317.
- [126] N. R. Pradhan, H. Duan, J. Liang, and G. S. Iannacchione, "The specific heat and effective thermal conductivity of composites containing single-wall and multi-wall carbon nanotubes," *Nanotechnology*, vol. 20, no. 24, pp. 245705-1-7, 2009.
- [127] X. C. Gui, K. L. Wang, J. Q. Wei, R. T. Lü, Q. K. Shu, Y. Jia, W. Chen, H. W. Zhu, and D. H. Wu, "Microwave absorbing properties and magnetic properties of different carbon nanotubes," *Science in China Series E Technological Sciences*, vol. 52, no. 1, pp. 227-231, 2009.
- [128] B. Window, and G. Harding, "Thermal emissivity of Copper," *Journal of the Optical Society of America*, vol. 71, no. 3, pp. 354-357, 1981.
- [129] S. M. Sze, and K. K. Ng, *Physics of Semiconductor Devices*, 3rd ed.: John Wiley & Sons, Inc., 2007.

- [130] S. J. Park, A. J. Schmidt, M. Bedewy, and A. J. Hart, "Measurement of carbon nanotube microstructure relative density by optical attenuation and observation of size-dependent variations," *Phys Chem Chem Phys*, vol. 15, no. 27, pp. 11511-9, 2013.
- [131] E. D. Palik, Handbook of Optical Constants of Solids: Elsevier, 1998.
- [132] P. Yaghoobi, M. Vahdani Moghaddam, and A. Nojeh, "Solar electron source and thermionic solar cell," *AIP Advances*, vol. 2, no. 4, pp. 042139, 2012.
- [133] K. G. Kreider, "Thin film transparent thermocouples," *1991 International Conference on Solid-State Sensors and Actuators (TRANSDUCERS)*, pp. 643-645, 1991.
- [134] D. Thuau, I. Koymen, and R. Cheung, "A microstructure for thermal conductivity measurement of conductive thin films," *Microelectronic Engineering*, vol. 88, no. 8, pp. 2408-2412, 2011.
- [135] D. Hohnholz, K.-H. Schweikart, and M. Hanack, "A Simple Method for the Subdivision of ITO Glass Substrates," *Advanced Materials*, vol. 11, no. 8, pp. 646-649, 1999.
- [136] S. K. Choi, and J. I. Lee, "Effect of film density on electrical properties of indium tin oxide films deposited by dc magnetron reactive sputtering," *Journal of Vacuum Science & Technology A*, vol. 19, no. 5, pp. 2043-2047, 2001.
- [137] F. Yi, E. Shim, A. Y. Zhu, H. Zhu, J. C. Reed, and E. Cubukcu, "Voltage tuning of plasmonic absorbers by indium tin oxide," *Applied Physics Letters*, vol. 102, no. 22, pp. -, 2013.
- [138] K. Sun, W. Zhou, X. Tang, Z. Huang, F. Lou, and D. Zhu, "Effect of the heat treatment on the infrared emissivity of indium tin oxide (ITO) films," *Applied Surface Science*, vol. 257, no. 22, pp. 9639-9642, 2011.
- [139] T. Margalith, O. Buchinsky, D. A. Cohen, A. C. Abare, M. Hansen, S. P. DenBaars, and L. A. Coldren, "Indium tin oxide contacts to gallium nitride optoelectronic devices," *Applied Physics Letters*, vol. 74, no. 26, pp. 3930-3932, 1999.
- [140] M. Kang, K. K. Kim, M. Chu, S. W. Kim, and K.-W. Ryu, "Optical Properties of Sputtered Indium-tin-oxide Thin Films," *Journal of the Korean Physical Society*, vol. 59, no. 5, pp. 3280-3283, 2011.
- [141] ASM Ready Reference: Thermal properties of metals: ASM International, 2002.
- [142] E. Talbot, A. Yousefpour, P. Hubert, and M. Hojjati, "Thermal behavior during thermoplastic composites resistance welding," *Proceedings of the Annual Technical Conference (ANTEC) of the Society of Plastics Engineers*, 2005.
- [143] L. Shi, D. Li, C. Yu, W. Jang, D. Kim, Z. Yao, P. Kim, and A. Majumdar, "Measuring Thermal and Thermoelectric Properties of One-Dimensional Nanostructures Using a Microfabricated Device," *Journal of Heat Transfer*, vol. 125, no. 5, pp. 881-888, 2003.
- [144] J. Liu, J. Sun, and L. Gao, "Flexible single-walled carbon nanotubes/polyaniline composite films and their enhanced thermoelectric properties," *Nanoscale*, vol. 3, no. 9, pp. 3616-3619, 2011.

## Appendix A

#### Effect of Compression

A side experiment was performed to observe if there would be any noticeable change in the induced voltage upon compression of the CNT forest. The device used here was a symmetric silicon-CNT-silicon sandwich. Shown in part (a) of Figure 57 below is the induced thermoelectric voltage as a function of applied temperature difference performed three times on the same pristine sample. In part (b), the effective Seebeck coefficient of the device was calculated as a function of average temperature. Upon compression of the CNT forest to approximately half of its original height, we observed a nearly doubling of the induced voltage at the same temperature difference, shown in part (c). Therefore, the effective Seebeck coefficient, shown in part (d), was almost doubled. Since the Seebeck coefficient has no geometric factor involved, we believe this voltage enhancement was simply due to better contact between the silicon contacts and the CNT forest.



Figure 57: Pristine Si-CNT-Si (a) potential difference vs. temperature gradient, (b) Seebeck coefficient vs. average temperature, compressed Si-CNT-Si (c) potential difference vs. temperature gradient, (d) Seebeck coefficient vs. average temperature

## Appendix B

#### COMSOL Longitudinal Conduction Model - Data

Table 10: Model 1 (reference room temperature material properties)

$Q_0 (\mathrm{mW})$	$\kappa_{\parallel} (W \cdot m^{-1} \cdot K^{-1})$	$\kappa_{\perp} (W \cdot m^{-1} \cdot K^{-1})$	$T_{H}(\mathbf{K})$	$T_{C}(\mathbf{K})$	$\Delta T(\mathbf{K})$	$T_{max}\left(\mathbf{K}\right)$	$\Delta V_{sim} (\mathrm{mV})$	$\Delta V_{exp} (\mathrm{mV})$
6.75	0.5	0.06	302.04	301.96	0.08	302.09	0.0018722	0
20.25	0.5	0.06	317.79	317.56	0.23	317.94	0.0056136	0
33.75	0.5	0.06	331.52	331.14	0.38	331.77	0.0093511	0
47.25	0.5	0.06	343.76	343.22	0.54	344.11	0.013088	0
67.5	0.5	0.06	360.00	359.23	0.77	360.50	0.018679	0
202.5	0.5	0.06	435.14	432.83	2.31	436.64	0.055797	0.040
270.0	0.5	0.06	461.81	458.74	3.07	463.81	0.074254	0.071
337.5	0.5	0.06	484.68	480.85	3.83	487.17	0.092649	0.096
405.0	0.5	0.06	504.84	500.25	4.59	507.83	0.11098	0.123
472.5	0.5	0.06	522.80	517.46	5.34	526.29	0.12929	0.148

Table 11: Model 2 (experimental room temperature material properties)

$Q_0$ (mW)	$\kappa_{\parallel} (W \cdot m^{-1} \cdot K^{-1})$	$\kappa_{\perp} (W \cdot m^{-1} \cdot K^{-1})$	$T_{H}(\mathbf{K})$	$T_C(\mathbf{K})$	$\Delta T(\mathbf{K})$	$T_{max}$ (K)	$\Delta V_{sim} (\mathrm{mV})$	$\Delta V_{exp} (\mathrm{mV})$
6.75	0.5	0.06	302.04	301.96	0.08	302.09	0.0012912	0
20.25	0.5	0.06	317.79	317.56	0.23	317.94	0.0038714	0
33.75	0.5	0.06	331.52	331.14	0.38	331.77	0.0064489	0
47.25	0.5	0.06	343.76	343.22	0.54	344.11	0.0090239	0
67.5	0.5	0.06	360.00	359.23	0.77	360.50	0.012882	0
202.5	0.5	0.06	435.14	432.83	2.31	436.64	0.038478	0.040
270.0	0.5	0.06	461.81	458.74	3.07	463.81	0.051204	0.071
337.5	0.5	0.06	484.68	480.85	3.83	487.17	0.063887	0.096
405.0	0.5	0.06	504.84	500.25	4.59	507.83	0.076529	0.123
472.5	0.5	0.06	522.80	517.46	5.34	526.29	0.089148	0.148

Table 12: Model 3 (experimental room temperature material properties, tuned thermal conductivity)

$Q_0$ (mW)	$\kappa_{\parallel} (W \cdot m^{-1} \cdot K^{-1})$	$\kappa_{\perp} (W \cdot m^{-1} \cdot K^{-1})$	$T_{H}(\mathbf{K})$	$T_C(\mathbf{K})$	$\Delta T(\mathbf{K})$	$T_{max}\left(\mathbf{K}\right)$	$\Delta V_{sim} (\mathrm{mV})$	$\Delta V_{exp} (\mathrm{mV})$
67.5	5	0.5	359.62	359.44	0.08	359.63	0.0014358	0
202.5	0.480	0.0480	435.22	432.82	2.40	436.75	0.040047	0.040
270.0	0.355	0.0355	462.70	458.39	4.31	465.34	0.071534	0.071
337.5	0.328	0.0328	486.08	480.28	5.80	489.62	0.096322	0.096
405.0	0.307	0.0307	506.83	499.43	7.40	511.33	0.12292	0.123
472.5	0.296	0.0296	525.32	516.40	8.92	530.74	0.14817	0.148

Table 13: Model 4 (reference and experimental temperature-dependant material properties, tuned thermal conductivity)

$Q_0$ (mW)	$\kappa_{\parallel} (W \cdot m^{-1} \cdot K^{-1})$	$\kappa_{\perp} (W \cdot m^{-1} \cdot K^{-1})$	$T_{H}(\mathbf{K})$	$T_C(\mathbf{K})$	$\Delta T(\mathbf{K})$	$T_{max}$ (K)	$\Delta V_{sim} (\mathrm{mV})$	$\Delta V_{exp}$ (mV)
67.5	8	0.8	359.50	359.45	0.05	359.61	0.0016438	0
202.5	1.082	0.1082	434.29	433.22	1.07	435.18	0.040036	0.040
270.0	0.806	0.0806	460.99	459.08	1.91	462.46	0.071110	0.071
337.5	0.744	0.0744	483.75	481.17	2.58	485.73	0.096203	0.096
405.0	0.695	0.0695	503.83	500.52	3.31	506.35	0.12342	0.123
472.5	0.675	0.0675	521.82	517.84	3.98	524.84	0.14824	0.148

# Appendix C

	1					
	Table	14: Model 5 (re	ference room t	emperature ITO n	aterial properties)	
$Q_0$ (mW)	$T_{H}\left(\mathrm{K}\right)$	$T_C(\mathbf{K})$	$\Delta T(\mathbf{K})$	$T_{max}$ (K)	$\Delta V_{sim} (\mathrm{mV})$	$\Delta V_{exp} (\mathrm{mV})$
28.4	365.18	363.32	1.86	365.19	0.16734	0.401
56.7	411.41	407.07	4.34	411.60	0.43953	0.687
85.1	446.96	440.11	6.85	453.73	0.78423	1.122
113.4	476.34	467.05	9.29	488.18	1.1887	1.668
141.8	501.70	489.95	11.75	518.36	1.6471	1.906
170.1	524.28	510.03	14.25	544.57	2.1563	2.441
198.5	544.71	527.96	16.75	565.86	2.7108	3.005
226.8	563.44	544.20	19.24	582.71	3.3077	3.554
255.2	580.73	559.03	21.70	596.59	3.9441	3.760
283.5	596.78	572.66	24.12	608.68	4.6164	4.285

### COMSOL Perpendicular Conduction Model – Data