Thermoelectric Generator based on Carbon nanotubes

By

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Abstract

Thermoelectric (TE) materials are used within devices that can be used to convert heat energy directly into electrical energy. When a temperature gradient is applied across a TE device, it is observed that an electrical potential is established. An efficient TE device requires a high figure of merit (ZT) which means a high power factor and a low thermal conductivity are necessary. In this project, Carbon Nanotubes (CNTs) were selected for investigation as an alternative to commercial TE devices made from Bismuth Telluride, mainly due to their availability, low carbon footprint, high design capability, mechanical flexibility, low manufacturing cost and potential for better device performance.

This work includes the fabrication process of CNT films which has been explored as well as doping them to n-type and p-type semiconductors. It also compares the effect of seven surfactants: Sodium dodecylbenzenesulfonates (SDBS), Sodium dodecyl sulfate (SDS), Pluronic F-127, Brij 58, Tween 80, Triton X-405 and Benzalkonium chloride (ABAC). These surfactants are categorised depending on their hydrophilic group polarity (anionic, non-ionic and cationic). Samples exposed to ambient oxygen were found to exhibit p-type behaviour, while the inclusion of Polyethylenimine (PEI) results in n-type behaviour. The highest output power from the TE devices made of a single pair of p and n-type elements was measured to be as high as 1.5 nW/K (67 nW for a 45K temperature gradient), which is one of the highest obtained. This was achieved with Triton X-405. In addition, the electrical data obtained revealed that Triton X-405 has the highest Seebeck coefficient with 81 µV/K and a conductivity of 3.7E+03 S/m due to its short hydrophobic end and non-polar hydrophilic tail which constitutes one of the novelties of this PhD. On the other hand, the anionic surfactant SDBS with its positive end showed a 55 µV/K but a significantly higher electrical conductivity at around 2.6E+4 S/m which is believed to be due to the contribution of additional carriers (sodium ions) from the surfactant. Thermogravimetric analysis (TGA) conducted on the surfactants confirm the maximum operating temperature of each surfactant by showing their thermal degradation points. With this, it was observed that Triton X-405 and Tween 80 indicated a thermal degradation point around 364 °C and very low residue left of around 0.12% compared to 33% and 25% for SDBS and SDS respectively.
In regard to the thermal behaviour of the CNT samples, it was revealed that CNT films with lengths above 1 cm showed heat losses due to emissivity, therefore, making longer films was deemed inefficient.

Finally, a TE device is made from the best performing surfactant (Triton X-405) because of its optimum power factor, with 6 pairs of p and n type semiconducting CNT films. This device was used for a motorcycle exhaust in order to simulate heat waste harvesting which resulted in a ~ 42 mV output voltage at ~ 87 °C temperature difference. This means that many alternating pairs of p-n devices are required to achieve a high output power.
Declaration of originality

I confirm that the submitted work is my own work and that I have clearly identified and fully acknowledged all material that is entitled to be attributed to others (whether published or unpublished). Any ideas, data, images or text resulting from the work of others are identified as such and attributed to the original author in the text, figure captions or the bibliography. I agree that the University may submit my work to means of checking this, such as the plagiarism detection service Turnitin® UK. I confirm that I understand that assessed work that has been shown to have been plagiarised will be penalised.

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Date: 25/01/2019
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“Thermoelectric properties of films based on carbon nanotubes”. Zakaria Saadi, José V. Anguita, Vlad Stolojan and S. Ravi P. Silva. (Oral presentation at the EMRS conference meeting, Warsaw, Poland, September 2016)

“Thermoelectric properties and PTCVD growth of CNTs”. Zakaria Saadi, José V. Anguita, Vlad Stolojan and S. Ravi P. Silva. (Oral presentation at ESPRC Thermoelectric Network UK Meeting, Glasgow, Scotland, October 2016)

Contents
Abstract ........................................................................................................................................... ii
Declaration of originality ................................................................................................................. iv
Acknowledgements ........................................................................................................................ v
Conference presentations ............................................................................................................. vi
List of Figures ............................................................................................................................... x
List of Tables .................................................................................................................................. xvi
Abbreviations and Acronyms ......................................................................................................... xvii
1 Introduction and objective ........................................................................................................ 1
  1.1 Background to the project .................................................................................................... 1
  1.2 Structure of the thesis ......................................................................................................... 5
2 Theory and literature review ....................................................................................................... 8
  2.1 Introduction ........................................................................................................................ 8
  2.2 Theory of thermoelectricity ............................................................................................... 9
  2.3 Figure of merit ZT (TE generation and Refrigeration efficiency) ..................................... 13
  2.4 Solid state materials: Metals, semiconductors and insulators ........................................ 18
  2.5 Fermi level ....................................................................................................................... 20
  2.6 Inorganic thermoelectric materials .................................................................................. 23
    2.6.1 Bismuth Telluride (Bi$_2$Te$_3$) and other materials ................................................ 23
  2.7 Organic thermoelectric materials ...................................................................................... 27
    2.7.1 Introduction to carbon nanotubes .............................................................................. 27
    2.7.2 CNT synthesis ........................................................................................................... 30
    2.7.3 CNT Properties ........................................................................................................ 34
    2.7.4 CNT dispersion/functionalization ............................................................................ 36
    2.7.5 Surfactant selection ................................................................................................... 38
  2.8 Optimisation of Thermoelectric properties ....................................................................... 41
    2.8.1 Increasing the power factor ...................................................................................... 41
    2.8.2 Minimising thermal conductivity .............................................................................. 42
  2.9 Applications of thermoelectric materials .......................................................................... 44
    2.9.1 Solar thermal energy generation ............................................................................... 47
  2.10 Summary ........................................................................................................................... 48
3 Characterisation techniques ........................................................................................................ 50
  3.1 Electrical conductivity measurement ................................................................................ 50
3.1.1 The Van der Pauw method ......................................................... 52
3.1.2 Transmission line measurement.................................................. 55
3.2 Seebeck coefficient measurement.................................................. 57
3.3 Scanning Electron Microscopy ....................................................... 67
3.4 Raman Spectroscopy ...................................................................... 68
3.5 UV-VIS Spectroscopy ..................................................................... 73
3.6 Thermogravimetric Analysis ............................................................ 75
3.7 Summary ......................................................................................... 76

4 CNT films fabrication and characterisation ....................................... 77
4.1 Characterisation of Thomas Swan CNTs ......................................... 77
  4.1.1 SEM analysis ............................................................................ 78
  4.1.2 TEM analysis ........................................................................... 80
  4.1.3 Raman analysis ........................................................................ 82
  4.1.4 TGA analysis of CNTs ............................................................... 85
4.2 p-type and n-type CNT films fabrication ......................................... 87
  4.2.1 Experimental procedure ............................................................ 90
4.3 Surfactant/CNT films characterisation ........................................... 94
  4.3.1 SEM analysis ............................................................................ 94
  4.3.2 Raman analysis ....................................................................... 96
  4.3.3 TGA analysis of surfactants and PEI ......................................... 104

5 Thermoelectric properties of CNT films ............................................. 107
5.1 Seebeck coefficient and electrical conductivity ............................ 107
5.2 TE device fabrication and characterisation .................................... 112
5.3 Selection of highest performing TE device (Triton X-405/CNT) ...... 117
5.4 Effect of doubling CNT mass on electrical conductivity............... 119
5.5 Summary ....................................................................................... 121

6 Conclusion and Future Work .......................................................... 122

Appendices ......................................................................................... 124

I Appendix A: VACNTs synthesis and characterisation ....................... 124
  I.I Introduction ................................................................................ 124
  I.II Description of PTCVD system ................................................... 125
  I.III Preparation of substrate and catalyst ......................................... 126
  I.IV VACNT fabrication using PTCVD ............................................. 129
List of Figures

Figure 1-1. Schematic diagram of waste heat recovery conversion into electricity displaying the energy lost at 66%, and only 34% of the energy is used by power plants, automobiles factories and gas fields, etc [5]. ........................................................................................................2

Figure 1-2. Schematic diagram of waste heat available in the human body and the amount of power each body part can generate. It is notable that the chest and abdomen produce the highest rate of power at about 36.6 mW during high activity [11]. .................................................. 3

Figure 2-1. The number of Publications per year in the field of thermoelectricity between 1990 and 2016. Reproduced from the Web of Science 2018. ................................................................. 8

Figure 2-2. Schematic diagrams showing TE device configurations: (a) n-type TE elements connected electrically and thermally in parallel, (b) n-type TE elements connected electrically in series at opposite ends and thermally in parallel. ............................................ 10

Figure 2-3. A typical thermoelectric module showing the flow of charge carriers for both power generation and cooling. Both electrons and holes diffuse from the hot end to the cold end. Reproduced from [9]. ........................................................................................................ 11

Figure 2-4. Set up diagrams for: (a) Seebeck effect, (b) Peltier effect. .......................................................... 12

Figure 2-5. Schematic diagrams for: (a) thermoelectric generator, (b) thermoelectric refrigerator ................................................................................................................................. 13

Figure 2-6. Efficiency of a TE generator for different ZT values [15]. .......................................................... 16

Figure 2-7. Dependence on of electrical conductivity, Seebeck coefficient and power factor on concentration of free carriers [16]. .................................................................................................... 19

Figure 2-8. Fermi distribution function plotted against $E-E_F/kT$ [1]. ................................................................. 21

Figure 2-9. Energy band diagram showing the valence and conduction bands separated by the Fermi level. ................................................................................................................................. 21

Figure 2-10. Schematic diagram of energy states for different solids: (a) insulator, (b) intrinsic semiconductor, (c) n-type semiconductor, (d) p-type semiconductor ........................................... 22

Figure 2-11. Crystallographic structure of Bi$_2$Te$_3$ by the stacking of cubes along the [111] direction [22]. ................................................................................................................................. 23

Figure 2-12. Overview of developed thermoelectric materials and their ZT values [12][15]. ......... 26

Figure 2-13. Schematic diagram for the density of states in bulk materials in 3D, 2D, 1D and 0D dimensionalities [30]. ........................................................................................................ 27

Figure 2-14. Schematic diagram highlighting the electronic density of states (DOS) for a semiconducting SWCNT. The sharp peaks represent the Van Hove Singularities (VHS) whereas the arrows show the energy difference between the sub bands [31]. ................. 29

Figure 2-15. (a) Schematic diagram of a plane graphene sheet which is rolled up to form a carbon nanotube. (b) Atomic structure of an armchair. (c) atomic structure of a zig-zag nanotube [36]. ................................................................................................................................. 30

Figure 2-16. Schematic diagram of the laser ablation method. A graphitic target mixed with a catalyst is hit by a high beam laser resulting in CNTs which are deposited on a collector [39]............................................................................................................................................. 31

Figure 2-17. Schematic for Arc-Discharge setup showing two electrodes where a high current is passed through [45]........................................................................................................ 32
Figure 2-18. CNT growth mechanism in CVD systems. It shows the carbon molecules diffusing around the metallic catalyst island which is the precursor of the CNT yield [50].

Figure 2-19. Schematic diagram for the CVD process for CNT synthesis. A hydrocarbon source interacts with a catalyst inside the reactor chamber with the help of a plasma or a thermal source like infrared lamps. The gases flow is controlled by a pressure gauge [51].

Figure 2-20. Schematic diagram showing the different mechanisms for the bonding of surfactants on the SWCNT surface: (a) Surfactant micelles encapsulating a SWCNT, (b) shows hemi-micellar absorption on the SWCNT, (c) Random formation/absorption of surfactant molecules on SWCNT [62].

Figure 2-21. Graph shows the critical micelle concentration point (CMC) [66].

Figure 2-22. Energy flow in internal combustion engines [4].

Figure 2-23. Schematic diagram of a STEG system made with thermoelectric elements (p-type and n-type semiconductors) and flat a panel on top which acts as a solar absorber (thermal concentrator) [90].

Figure 3-1. Schematics of Van der Pauw configurations for sheet resistance showing the different combinations [104].

Figure 3-2. (a) Schematic diagram for Van der Pauw measurement sample holder, (b) measurement rig where sample is placed on top of the black square holder and the four external pin connectors are used to make good electrical contact [104].

Figure 3-3. Metal contacts configuration for the TLM method, different spacings are used between the metal strips for accurate measurements [107].

Figure 3-4. Typical graph of resistance showing the TLM method for various contact separations. The data from the graph determines: \( T_t = \) transfer length, \( R_C = \) contact resistance, \( R_S = \) sheet resistance [107].

Figure 3-5. Calibration of the TLM method by measuring the resistivity of palladium showing two different thicknesses.

Figure 3-6. (a) Previous electrical probe used for the old setup. The benefit from using it was the ability to lower the probe using the right hand knob. This allows to carefully control the pressure put on the CNT sample, (b) Image showing spring loaded probes manually controlled to prevent damage to the CNT films if they are in direct contact.

Figure 3-7. (a) Schematic diagram showing the components used for the Seebeck measurement of the new setup, (b) measurement rig includes a vacuum chamber and multiple crocodile clips to be connected for powering up the platinum resistors, as well as voltage Mueller clips for recording potential differences across the CNT samples, plus thermocouples for temperature recording, (c) example of CNT samples placed on a glass slide for better handling where copper tapes and silver epoxy are used to electrically and thermally connect the CNT samples.

Figure 3-8. Data shows the temperature differences (\( \Delta T_1 \) to \( \Delta T_5 \)) for p-type Pluronic F127/CNT within a range varying between 7 to 18 °C acquired using the Pico Data Logger TC-08. The steady state is reached after ~ 480 Seconds.

Figure 3-9. Calibration of the Seebeck test rig showing two different setups: the old setup and the new setup. The New system shows an increase and a closer value of the Seebeck coefficient to the reported ones. The gradient is displayed which corresponds to the Seebeck coefficient.
Figure 3-10. Linear gradient for 5 data points displaying the Seebeck voltage as a function of temperature difference across a p-type CNT/SDBS film. The resulting Seebeck coefficient value is ~ 54.4 µV. .......................................................... 64

Figure 3-11. Schematic diagram highlighting the heat transfer as a function of separation between the hot side and the cold side................................................................. 65

Figure 3-12. (a) Plot showing absolute temperature for p-type CNT films as a function of separation; the temperature gradient drops from ~ 40 °C/cm to around ~ 5 °C/cm after 1cm. (b) Plot displays Seebeck coefficient values vs separation which shows linear drop for most surfactants indicating that the charge carriers diffusion to the cold end is strongly affected by the length due to the increase in contact resistance between individual tubes. .......................................................... 66

Figure 3-13. (a) Thermal imaging of the CNT film illustrates the heat transfer along the sample, (b) temperature profile of the CNT film obtained using ImageJ. The RGB values are converted to grey-scale before a line profile is taken. The arrow indicates the start of the CNT film. .................................................................................................. 66

Figure 3-14. SEM micrographs displaying CNT films dispersed using SDS: (a) cross Section area of CNT/SDBS film showing a uniform CNT film due to CNTs stacked on each other in a random manner, (b) high magnification (90000x) image of randomly distributed CNTs.................. 68

Figure 3-15. Raman energy diagram illustrating the phonon interaction with an electron resulting in three types of scatterings: (a) Rayleigh scattering where the excited electron is scattered immediately falls to the ground level, (b) Stokes scattering where the excited electron emits photon and falls to the vibrational state, (c) Anti-Stokes scattering where the excited electron goes form the vibrational state to the ground state [120]. ................. 69

Figure 3-16. SWCNT Raman signals displaying various peaks: RBM region for determining CNT diameter, Silicon peak used as a reference point, D peak corresponds to the defective sites within the CNTs, G peak related to the graphitic content of CNTs [35]............................ 71

Figure 3-17. Typical Raman signal measured using the Raman Renishaw where all the peaks are in agreement to with the reported Raman signals by Dresselhaus. ................................................. 72

Figure 3-18. A typical Kataura plot displays the relationship between the energy separation and the nanotubes diameter (SWCNTs). The red and blue dots refer to semiconducting and metallic SWCNTs respectively. The red and green lines correspond to the laser energies available for the Raman Renishaw [128][131]. ................................................... 73

Figure 3-19. Schematic diagram of typical spectrometer, a light source is passed through a monochromator which splits photons by wavelength, which then goes through the sample and the altered light is monitored by the detector [132]. ......................................................... 74

Figure 3-20. Diagram of integrating sphere highlighting diffuse reflectance and all the components used for optically characterising a VACNT sample as seen in Appendix A........... 74

Figure 4-1. CNT film that has been filtered on a PTFE membrane with no surfactant content showing some cracks on the sample............................................................. 78

Figure 4-2. SEM image of a CNT film with no surfactant content; (a) cross Section area of the CNT film showing CNTs stacked next to each other and the red circles highlighting impurities and/or catalyst particles, (b) Higher magnification of the CNTs showing bundles of CNTs.............................................................................................................. 79

Figure 4-3. TEM images of Thomas Swan CNTs showing double walled CNTs, (b) (c) zoomed in areas of DWCNTs displaying their diameters, (d) low contrast TEM image which doesn’t indicate any impurities or iron catalyst particles. Reproduced from [141]................................. 81
Figure 4-4. Raman spectrum of CNT film acquired from red laser 782 nm shows a typical Thomas Swan CNT sample with a D-G ratio of 0.15 displaying the regions of interest and key peaks. ................................................................. 82

Figure 4-5. (a) RBM region where each peak is used to identify the different CNT diameters, (b) G peak splitting modelled using a Lorentzian function where the fitted curves show 3 G’ and 1 G”, indicating DWCNT. ........................................................................................................ 85

Figure 4-6. TGA graph obtained from ~ 7 mg of CNTs from a batch produced by Thomas Swan and Co. Ltd, measured in air with 92.35% water content and only ~ 7% CNT weight fraction and ~ 0.8% residual mass. ........................................................................................................ 87

Figure 4-7. Chemical structure of the surfactants used in these experiments for dispersing the CNTs; non-ionic surfactants (SDBS and SDS) contain a hydrophobic chain of 10 hydrocarbons (CH₂). Triton X-405 has the shortest hydrocarbon chain among non-ionic surfactants, whereas Tween 80 and Pluronic F-127 have the longest chains and B58 has 14. ADBAC can have long hydrophobic chains depending on “n” value which can range from 8 to 18................................................................. 90

Figure 4-8. CNTs were dispersed with and without a surfactant for a visual comparison on how dispersed and non-dispersed CNTs appear after sonication; dispersed CNTs (right), Non Dispersed CNTs (left) ........................................................................................................ 91

Figure 4-9. Experimental procedures for obtaining a CNT film; (a) probe sonicator used to disperse CNTs while allowing surfactant particles to adhere to the CNT outer structure, (b) Hot plate to heat up the beaker and a temperature probe immersed into the solution to accurately obtain the desired 55 °C, (c) a vacuum filter system where the solution is poured into the Buchner funnel to obtain a CNT film, (d) a circular shape CNT film that can be cut into specific dimensions. ........................................................................................................ 93

Figure 4-10. SEM micrographs displaying CNT films dispersed using SDBS: (a) cross Section area of CNT/SDBS film showing a uniform network of CNTs stacked on each other in a random manner, (b) image of CNTs from CNT/SDBS film, (c) cross Section area of CNT/SDBS/PEI film showing PEI infused CNT film resulting in a thicker film, d) image of CNTs from CNT/SDBS/PEI film........................................................................................................ 95

Figure 4-11. Graph displaying the I₀/I₈ ratio of the CNT films (open symbols are for p-type CNTs and closed symbols are for n-type CNTs); the low values obtained are a strong indication of good quality CNTs. SDBS p-type film shows the lowest ratio due to the low density of defects. ADBAC p-type film has the highest ratio, but when adding PEI, the I₀/I₈ ratio drops significantly meaning that PEI acted as a binding chemical agent............................................ 97

Figure 4-12. Plot showing G peak position of raw CNTs and CNT films (open symbols are for p-type CNTs and closed symbols are for n-type CNTs), for Non-ionic and cationic surfactants a red-shift in frequency is observed when comparing p-types to n-types. Additionally, when looking peak frequency shift of the raw CNTs compared to the CNT/surfactant samples, we can see a red-shift which prove that the CNTs have been dispersed. ............................................ 99

Figure 4-13. Raman spectra of seven surfactants (both p-type and n-type semiconductors) at the RBM region of the samples aligned against each other shows roughly the same peak positions as the raw CNTs which indicates that it is the same CNTs coming from the same batch; this is expected because the RBM corresponds to the vibrations in the radial direction of the carbon atoms, so any functionalization using surfactants happens on the outer shell of the tubes, thus, it should have no impact on the diameter of the CNTs...... 101
Figure 4-14. Ratio DWCNT shells of the inner to outer wall (open symbols are for p-type CNTs and closed symbols are for n-type CNTs). A higher ratio means a higher intensity of the inner wall compared to the outer wall, meaning that the inner walls are undamaged and vice versa. .................................................................................................103

Figure 4-15. TGA data for non-ionic and anionic surfactants used to disperse the CNTs, analysed in both air and Nitrogen environments. Non-ionic surfactants produced the best results with Triton X-405 producing the least amount of residue in air at 0.12%. Anionic surfactants left the largest amount of residual masses due to their sodium contents [141]. ..................105

Figure 4-16. TGA data analysed in both air and Nitrogen environments for PEI used as a dopant to functionalize dispersed CNTs into n-type semiconductor material ..................................106

Figure 5-1. Column graph of the Seebeck coefficient as a function of CNT films for two main categories of surfactants, anionic and non-ionic. SDBS and SDS CNT films show low values due to their high concentration of charge carriers. Triton X-405 CNT films show the highest values due to their low carrier concentration and large effective mass which is discussed in Section 5.2 ........................................................................................................109

Figure 5-2. (a) Column graph of the electrical conductivity (Van der Pauw) as a function of CNT films for two main categories of surfactants, anionic and non-ionic. SDBS and SDS CNT films show the highest values due to their high concentration of charge carriers because of the sodium ions. All the non-ionic surfactant CNT films show significantly lower values due to their low carrier concentration, (b) shows the comparison between the Van der Pauw method (black bars) and TLM method (red bars) showing that the TLM line may also be used to estimate the electrical conductivity .................................................................110

Figure 5-3. Plot of power factor as a function of CNT films. SDBS shows the highest power factor due to its high electrical conductivity. Triton X-405 is the highest among non-ionic surfactant due to its high Seebeck coefficient and electrical conductivity .......................111

Figure 5-4. (a) Schematic diagram of a TE device made of a p-n type semiconductors displaying the arrangement of the TE elements which are connected electrically in series and thermally in parallel, (b) a TE device made of CNT/Triton X-405 composite films showing the platinum resistors which are used to control and maintain a steady temperature gradient........................................................................................................113

Figure 5-5. A graph displaying the output power for the surfactant CNT films as a function of resistance at a temperature difference of 45 K. The highest value is represented by Triton X-405 due to its high Seebeck coefficient and low residual content .......................115

Figure 5-6. (a) A TE device made of 6 pairs of p-n semiconductors obtained from dispersing CNTs in Triton X-405 then placed on a semi-circular MDF for better handling, (b) TE device used for generating 41.9 mV at ~ 91 °C temperature difference on an exhaust pipe of a motorcycle ........................................................................................................119

Figure 5-7. A plot highlighting the electrical conductivity for p-type CNT films functionalized with the surfactants. It shows the effect of doubling the mass on the electrical conductivity. ..................................................120

Figure I-1. Schematic diagram of the Photo-thermal CVD system 1000N includes; 8 IR lamps covered by a quartz glass, a substrate holder located above the water cooling line, an inlet for the reactant gases, and a pump [179]. ...........................................................................125

Figure I-2. Structure of the substrate layers, TiN is deposited on n-type silicon wafer which acts as a thermal barrier, followed by an aluminium layer and its native oxide which is sputtered and acts as an anchor layer. Lastly, the Fe catalyst is deposited on top of the native alumina ........................................................................................................127

xiv
Figure I-3. Graph shows: (a) Reflectance of 25 nm aluminium where over 90% of IR light is reflected to enhance CNT growth [190], (b) Transmittance of 5 nm aluminium oxide where over 90% of IR is transmitted which in turn reaches the reflective layer (aluminium) [192].

Figure I-4. Optical Images of CNTs grown on silicon wafer at powers of: (a) SAM1 = 47.5%, (b) SAM2 = 50%, (c) SAM3 = 52.5% and d) SAM4 = 55% display very high absorbing properties due to their very dark (black) surface.

Figure I-5. Graph shows the absorptivity of VACNT forest (red, blue, pink and black line) and a standard black paint on a plastic surface (green line) of 0.5 cm in thickness. The noise at around 800 nm is a caused as a result of a change in the detector/filter speed reading when measuring in the near-infrared range. The absorption is estimated from the reflection geometry only (A = 1 – R).

Figure I-6. Reflectance characterisation of VACNT forests (SAM1, 2, 3 and 4) using the integrating sphere. The spectra is dominated at the 800 nm mark for a short range by artefact.

Figure I-7. SEM for VACNTs showing a very dense CNT forest closely packed together (bundles) which results in an extremely low reflectance, thus, a higher absorption.

Figure I-8. CNT growth model by Robertson displaying the tow different growth models, the carbon and hydrogen atoms are coloured in blue and white respectively and the black lines represent the CNT walls (a) A tip growth where the carbon molecules diffuse around the catalyst resulting in the CNT lifting off the catalyst particle, as oppose to the root growth, (b) shows a diffusion process through the catalyst [203].

Figure I-9. SEM images of the VACNTs grown at two different temperatures ranging (380 - 490 °C) with two different TiN layer thicknesses (50 nm and 100 nm).

Figure I-10. Raman spectrum of a typical VACNT signal synthesized using the PTCVD 1000N with a D-G ratio of 0.10 displaying the regions of interest and key peaks such as RBM, D and G peaks, and 2D.

Figure I-11. I_D/I_G ratio as a function of set power for VACNT growth. The data shows that the thick reflective surface of TiN improves the quality of the CNTs.

Figure I-12. Growth rate of VACNTs as a function of temperature. The highest rate is attributed to the 100 nm TiN layer at 440 °C.
List of Tables

Table 2-1. Equation parameters and their definition. ................................................................. 14
Table 2-2. Experimental results on bulk materials and their properties [22]............................ 25
Table 4-1. List of surfactants from three different categories depending on the polarity of their hydrophilic ends: anionic with negative charge, cationic with positive charge and non-ionic with no apparent charge. ........................................................................................................ 89
Table 4-2. CNT films thickness for both p-type and n-type semiconductors. N-type films are thicker than the p-type samples due to the inclusion of PEI polymer which has a larger molecular chain. ................................................................................................................................................................................................. 95
Table 5-1. Comparison of triton X-405 performance against reported values by different groups. ........................................................................................................................................................................................................................................... 116
Table II-1. Raw data collected using the Van Der Pauw method for measuring the sheet resistance and computing the electrical resistivity from the CNT film thicknesses. .............. 144
### Abbreviations and Acronyms

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>Seebeck coefficient</td>
</tr>
<tr>
<td>σ</td>
<td>Electrical conductivity</td>
</tr>
<tr>
<td>ρ</td>
<td>Electrical resistivity</td>
</tr>
<tr>
<td>κ</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Aluminium oxide (Alumina)</td>
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<td>Argon</td>
</tr>
<tr>
<td>Bi₂Te₃</td>
<td>Bismuth Telluride</td>
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<td>Polyethylene glycol hexadecyl ether</td>
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<td>Catalytic chemical vapour deposition</td>
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<td>Longitudinal acoustic</td>
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<tr>
<td>LO</td>
<td>Longitudinal optical</td>
</tr>
<tr>
<td>MDF</td>
<td>Medium Density Fibreboard</td>
</tr>
<tr>
<td>m-SWCNT</td>
<td>metallic single wall carbon nanotubes</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi wall carbon nanotube</td>
</tr>
<tr>
<td>N₂</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
</tr>
<tr>
<td>NPL</td>
<td>National Physical Laboratory</td>
</tr>
<tr>
<td>PECVD</td>
<td>Plasma enhanced physical vapour deposition</td>
</tr>
<tr>
<td>PEI</td>
<td>Polyethyleneimine</td>
</tr>
<tr>
<td><strong>Pluronic F-127</strong></td>
<td>Poloxamer</td>
</tr>
<tr>
<td>PTCVD</td>
<td>Photo-thermal chemical vapour deposition</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical Vapor Deposition</td>
</tr>
<tr>
<td>RBM</td>
<td>Radial breathing mode</td>
</tr>
<tr>
<td>SDBS</td>
<td>Sodium dodecylbenzenesulfonate</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium dodecyl sulfate</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>SiC</td>
<td>Silicon carbide</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Silicon dioxide</td>
</tr>
<tr>
<td>SiOₓ</td>
<td>Silicon oxide(s)</td>
</tr>
<tr>
<td><strong>s-SWCNT</strong></td>
<td>Semiconducting single wall carbon nanotube</td>
</tr>
<tr>
<td>STEG</td>
<td>Solar thermoelectric generator</td>
</tr>
<tr>
<td>SWCNT</td>
<td>Single wall carbon nanotube</td>
</tr>
<tr>
<td>TE</td>
<td>Thermoelectric</td>
</tr>
<tr>
<td>TEG</td>
<td>Thermoelectric generator</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>TiN</td>
<td>Titanium Nitride</td>
</tr>
<tr>
<td>TLM</td>
<td>Transmission line measurement</td>
</tr>
<tr>
<td>tpp</td>
<td>Triphenylphosphine</td>
</tr>
<tr>
<td>Triton X-405</td>
<td>Polyethylene glycol tert-octylphenyl ether</td>
</tr>
<tr>
<td>Tween 80</td>
<td>Polyethylene glycol sorbitan monooleate</td>
</tr>
<tr>
<td>VACNT</td>
<td>Vertically aligned carbon nanotube</td>
</tr>
<tr>
<td>VHS</td>
<td>Van Hove singularities</td>
</tr>
<tr>
<td>ZT</td>
<td>Dimensionless Thermoelectric figure of merit</td>
</tr>
</tbody>
</table>
1 Introduction and objective

1.1 Background to the project

The increasing number of today’s world population and the decrease in fossil fuel supplies have caused a significant increase in energy demand. This has prompted Governments and research institutions to actively pursue alternative and clean energy sources as well as ways to harvest wasted energy. One way to achieve this is by exploring the use of advanced functional materials. However, there are many considerations to think of such as: protecting the environment, efficient processing techniques, increased strength and lightweight materials. An area of choice for modern applications would be thermoelectrics.

A thermoelectric (TE) device is an energy conversion device that uses the Seebeck effect to produce a voltage difference when there is a temperature gradient across the device. In an analogous manner, the Peltier effect is the generation of a heat flow (the presence of heating or cooling) when current is passed through the device [1].

Due to high demand in energy converting materials, TE devices have drawn a broad attention over the past few decades from various researchers, mainly because of their ability to convert heat into electricity or vice versa. It is estimated that over 60% of the energy is lost worldwide in the form of waste heat primarily [2]. This increase in demand has in turn raised the need for a practical solution that can be used for various applications, which can be utilized in different shaped components, hence the need for flexible materials.

In addition, TE devices are becoming increasingly important due to their potential applications in energy harvesting from conventional heat-based processes. For example, conventional thermal power stations and solar panels operate at an efficiency of 30-40%, which means that the energy that is primarily lost by heat is estimated to account for 2/3 of the overall energy produced [3]. Furthermore, internal combustion engines in both hydrocarbon and hybrid electric vehicles utilize only 25% of the fuel’s energy, resulting in 75% wastage through heat loss, mainly in the form of exhaust gas [4]. Thus, TE devices provide an important solution where waste heat can be harvested and then converted into electricity. Figure 1-1 describes the energy lost in the form of waste heat where only a 1/3 is used.
The performance of a TE module depends on the **Figure of merit**, $ZT = \frac{\alpha^2 \sigma}{\kappa} T$, where $\alpha$, $\sigma$, $\kappa$, and $T$ are the Seebeck coefficient, the electrical and thermal conductivity of the material and temperature difference, respectively. Current materials used in TE devices include Bismuth Telluride (Bi$_2$Te$_3$). These have high figure of merit values, with $ZT \approx 1$ [6]. In contrast, TE devices based on carbon nanotubes (CNTs) are reported to have a $ZT$ value $\approx 0.02$ [7]. This is significantly lower than those measured in Bi$_2$Te$_3$. However, the advantages of using CNT materials include flexibility, low cost of production and non-toxicity (when embedded into a solid matrix). In addition, CNTs are inherently low-dimensional, therefore, enabling the possibility to introduce nanoscale designs and nanoparticles that produce quantum confinement effects. These can be used to increase the $ZT$ value by enhancing the three interrelated parameters including a high electrical conductivity and Seebeck coefficient, as well as a low thermal conductivity ($\kappa$) [8][9].

The potential for flexible TE devices can be particularly useful if used on curved surfaces such as the human body. The latter can produce heat from the metabolic chemical reactions that take place. The body heat that arise from that reaction is a result of the conversion of organic matter into useful energy [10]. This causes the heat to be transferred to different parts of the
human body by blood flow which will then be released via radiation through the skin which is highlighted in Figure 1-2.

![Figure 1-2. Schematic diagram of waste heat available in the human body and the amount of power each body part can generate. It is notable that the chest and abdomen produce the highest rate of power at about 36.6 mW during high activity [11].](image)

Part of this project was to explore the electronic properties of CNTs by synthesising them using a photo-thermal chemical vapour deposition technique (PTCVD). On top of that, analysing their optical properties and structural configuration by looking at their Raman signal. However, the primary aim of this project was to fabricate a fully working, flexible and low cost thermoelectric generator (TEG) that can be set up in a way to allow maximum temperature gradient between the hot side and the cold side and converting this into a potential difference where thermoelectric (TE) elements are based on semiconducting CNTs. This TE device was then demonstrated as an application in a motor vehicle exhaust system which produces relatively high levels of waste heat, resulting in a high output voltage.

The CNT path taken for this project is due to the low-dimensionality structure of carbon nanotubes. In 3D crystal solids, the three ZT parameters are interrelated which makes it difficult to independently control all three properties. Therefore, if the dimensionality is reduced, then the variable of length scale would allow the control of the electrical and thermal properties of a material [8]. In other words, as the size is significantly decreased to the nanometer scale, dramatic changes can occur in the density of states which allows the introduction of quantum confinement by introducing nanoscale constituents in order to enhance the power factor ($\alpha^2\sigma$). From the literature, many have investigated the idea of
decoupling the electronic Density of States (DOS) from the phonon DOS and thereby boosting the ratio of the electrical conductivity to thermal conductivity ($\sigma/\kappa$) [12][13]. So, if this can be achieved on materials with a high Seebeck coefficient, then a high ZT can be significantly higher. This concept of increasing the power factor will be discussed and analysed further in Chapter 5.

Additionally, reducing the thermal conductivity is another requirement in order to obtain a high ZT value which can be achieved by scattering of phonons; this will prevent a significant amount of heat from flowing down across the TE elements where a temperature gradient exists. However, characterising the thermal conductivity parameter was deemed to be a complicated process. We attempted to measure the thermal conductivity by designing a steady state rig adapted for thin films. However, this has proved very complicated by the fact that the film is a random network of CNTs and the CNTs are very emissive (nearly perfect blackbodies). Nevertheless, some very important design conclusions can be drawn from examining the heat flux of the films (see Section 3.2). On the other hand, the power factor proved to be a good measure of the efficiency of the films, so, we concentrated on measuring it and finding ways to improve the power factor and investigate in detail the effect of surfactants’ bonding onto the outer structure of CNTs and on the output power performance of TE devices made of CNT films.

This work involves for the first time a systematic comparison between CNT films manufactured using different surfactants, which lead to different electrical behaviour, depending on the surfactant’s hydrophilic end polarity (positive, negative and neutral) and direction of the dipole. A surfactant’s main advantage is to offer a non-covalent type of functionalization, allowing the interaction between its hydrophobic part to bond with the CNTs outer wall due to Van der Waal forces making them more soluble and less prone to aggregate [14]. Furthermore, the data obtained from Raman spectroscopy revealed high quality CNTs, with small variations in the D (defect) peak after functionalisation, as shown in Section 4.3.2, which indicates that the surfactant-tube interaction is non-covalent.

Further to this, the dispersion efficiency was characterised by analysing the G (graphitic peak Raman wavenumber position, where a shift was noticed for all surfactants/CNT composites as a comparison to a non-functionalized CNT film. The shift in the G peak indicates that the CNTs are coated with surfactant molecules and we also suggest that this is an indication of the efficiency of dispersion.
Finally, by measuring the Seebeck coefficient and electrical conductivity, we show, for the first time, that the optimum power factor is achieved via the non-ionic surfactant (no polarity) Triton X-405; this gave the best performing TE device, generating ~ 1.5nW/K. In addition to its neutral charge, Triton X-405 molecules have the shortest hydrophobic end compared to the rest of the surfactants used for this project, which was correlated to a high Seebeck coefficient and a relatively high electrical conductivity. This has resulted in the highest output power which signifies that a short molecule reduces the tube-tube distance, thus, increasing the conductivity.

1.2 Structure of the thesis

The thesis is organised as follow:

**Chapter 2** discusses the theory behind thermoelectricity required to understand the ZT parameters as well as the literature review which covers a description of the actual TE devices that are available commercially most notably Bi₂Te₃. This is followed by an exploration of the CNTs and their different synthesis techniques, their properties and how to functionalize and disperse them. Furthermore, this chapter will also include an analysis on the categories of surfactants used to functionalize CNTs.

**Chapter 3** covers the characterisation techniques used for measuring the Seebeck coefficient and electrical conductivity of the CNT films produced. In addition, SEM (scanning electron microscopy), optical spectroscopy (for the as-grown CNTs using PTCVD), Raman measurements and Thermogravimetric analysis (TGA) were all used for this project.

**Chapter 4** explores the properties of Double wall CNTs (DWCNTs) synthesised by Thomas Swan and the fabrication process of the CNT films. This chapter will include:

- Characterisation of non-functionalized (pristine) DWCNTs used for this project which includes SEM, TEM and Raman analysis.
- Detail description of the functionalization and dispersion of the CNTs into p-type (air exposed) and n-type (mixed with PEI) using 7 surfactants (Anionic, non-ionic and cationic as well as the experimental process to obtain the CNT films after vacuum filtration.
- Analysis of the CNT films by observing the CNTs and the thickness of the CNT films.
- Acquiring the Raman signals for all CNT films functionalized in order to understand further the effect of the surfactants on the CNTs.

Chapter 5 explores the electrical performance of the fabricated TE devices which includes:
- Measurement of the Seebeck coefficient and the electrical conductivity of CNT films followed by the design of a TE device made of a p-type and n-type CNT films. The TE device characterisation includes the output power generated as a function of resistance. TGA of each surfactant will also be included in order to estimate the maximum operating temperature for the surfactants before reaching thermal degradation, which would affect the integrity of the CNT films.
- Furthermore, the best performing TE device is selected so that the final TEG (12 TE elements) is constructed and was used as an application for a motorcycle exhaust to simulate a temperature difference.
- Finally, a comparison of the electrical conductivity between the p-type CNT films (CNT mass = 18.7 mg) used to make the TEG device and new samples of p-type CNT films (CNT mass = 37.4 mg). The purpose of this experiment was to understand the effect of doubling the CNT mass, thereby, obtaining a thicker CNT film, on the electrical properties.

Chapter 6 summarises the thesis by outlining the achievements made throughout this PhD project. A brief discussion is also included on potential future ideas for this research which could arise as a result of this PhD.

In addition to the chapters mentioned above, various figures and details were also added to this thesis as Appendices. Appendix A discusses the growth of vertically-aligned CNTs (VACNTs) using the Photo-thermal chemical vapour deposition PTCVD technique. It includes details regarding substrate (silicon wafer) preparation, the different layers necessary for CNT growth and the iron (Fe) catalyst deposition. Furthermore, optical and Raman analysis was done on VACNT samples in order to assess their properties. However, this experimental work was carried out on the idea of using CNTs grown with a PTCVD process, but there were many
challenges that have been faced which prevented this path to be followed, thus, commercial CNTs (Thomas Swan) have been used instead. Therefore, some of the difficulties encountered using this growth technique are discussed in the Appendix A.
2 Theory and literature review

2.1 Introduction

The concept of thermoelectricity was first discovered in 1821 by Thomas J. Seebeck who first observed the behaviour of a needle of a compass that was deflected when in close proximity to two joined metallic conductors [15]. The junction connecting the two materials was exposed to various temperatures, therefore the degree of deflection away from the vicinity of the joint was observed to be proportional to the temperature gradient. It was believed that the reason for the needle’s movement was due to the electrical field created at the junction between the conductors by the temperature difference. The opposite effect was also discovered later on in 1834 by Jean C. A. Peltier: a current is applied to two conductors which results in a (negative) temperature difference. Thus, heat is transferred from one point to the other causing a cooling effect. Since then, research in the field of thermoelectricity has seen a significant increase. Figure 2-1 displays the number of publications from 1990 to 2016 which shows the significant worldwide adoption and activity in this area of physics by research institutions.

![Figure 2-1. The number of Publications per year in the field of thermoelectricity between 1990 and 2016. Reproduced from the Web of Science 2018.](image-url)
2.2 Theory of thermoelectricity

The thermoelectric effect consists of heating the junction between two dissimilar electrical conductors resulting in the production of an electromotive force. This phenomenon arises due to the difference in the free movement of charge carriers (carrying charge and heat) in metals and semiconductors. When a temperature difference exists between the junction and the circuit-ends of the materials, the majority carriers (electrons for n-doped and holes for p-doped) diffuse from the hot end to the cold end, where the charge carriers build up, producing a voltage. This is known as the Seebeck effect, which is the basis of thermoelectric power generation. Electrons and holes thermodynamically diffuse to the cold end seeking thermal equilibrium, therefore, an electric field builds up. However, at higher temperatures, the periodic collective excitations of a material’s atoms (phonons) will interact with electrons and cause carrier scattering, thus, as the electron scattering increases, the mobility decreases. In conclusion, it is ideal to operate at a relatively low average temperature, but a high temperature gradient.

A thermoelectric device can have multiple arrangements, with the goal being to increase the output voltage. As seen in Figure 2-2 (a), this configuration can consist of two n-type TE elements electrically and thermally in parallel. The drawback in this design is the generation of a low potential difference with high current. Another configuration can be observed in Figure 2-2 (b) where two n-type TE elements are electrically connected in series at opposite ends, and thermally in parallel. This arrangement presents a disadvantage in that, it allows a larger heat transfer across the interconnect, thus, reducing the charge transfer from the hot side to the cold side and the efficiency of the device. Therefore, the solution to this problem is using n-type and p-type semiconductors in order to form a thermocouple and increase the potential difference. Furthermore, if a thermocouple is made of homogenous materials, then no electromotive force can be produced because the Seebeck coefficient would be identical as seen in the following equation:

\[
\frac{dE_{AB}}{dT} = \alpha_A - \alpha_B
\]

Equation 2-1
A common TE device consists of two thermoelectric elements (n-type and p-type) connected electrically in series and thermally in parallel where the formation of a p-n junction and therefore a barrier to conduction is prevented by using an electrical conductor, as shown in the inset of Figure 2-3. In other words, a direct connection between an n-type and a p-type material would result in a diode, therefore, creating a depletion region at the junction where current can only pass in one direction.

This is considered the most efficient type of arrangement since it allows the thermoelectric elements (p and n type semiconductors) to simultaneously be heated from one side in order to thermally diffuse the charge carriers to the cold end. At the same time, the electrical series configuration results in an open circuit with positive and negative electrodes as if it was a battery where the higher the number of pairs (p and n), the higher the output power. Furthermore, in order to obtain the maximum chemical potential difference due to the build-up of charges at the cold side, two different types of charge carriers are necessary (electrons and holes).

This typical TE device shown in Figure 2-3 powers an electrical load via an external circuit by absorbing heat that creates a temperature difference between the top surface and bottom surface which provides a voltage induced by the Seebeck effect [9].

Figure 2-2. Schematic diagrams showing TE device configurations: (a) n-type TE elements connected electrically and thermally in parallel, (b) n-type TE elements connected electrically in series at opposite ends and thermally in parallel.
In addition to power generation which is obtained from the Seebeck effect, the Peltier effect is the reversible process, and is used in thermoelectric refrigeration. This consists of the drift of electric charge via a potential difference to produce a heat flow, thereby creating heating and cooling effects, depending on the direction of the electric current.

These two thermoelectric effects are shown in Figure 2-4. Here, two dissimilar conductors electrically connected in series, A and B, are joined together and exposed to a temperature difference $\Delta T$ as seen in Figure 2-4 (a), where an output voltage $V_{ab}$ is generated.

On the other hand, when an electric current flows from material A to B then to material A, as shown in Figure 2-4 (b), it results in different kinetic energies of the charge carriers within the materials at either side of the junctions. At junction 1, heat $Q_P$ is absorbed from the surroundings, whereas at junction 2, at least (accounting for heat losses) the same amount of heat is emitted.
By defining the Seebeck and Peltier coefficients, the relationship between these two effects can be discussed. Firstly, the Seebeck coefficient (α) also known as the thermopower (S) is defined as the ratio of the voltage generated across the device to the temperature difference across the device:

$$\alpha = \frac{V}{T_1 - T_2}$$  \hspace{1cm} Equation 2-2

α can be positive or negative, where the direction of the current flow determines the sign. If the flow is from conductor A to conductor B at the hot junction (Figure 2-4 (a)), then α is positive and vice versa. The type of charge carriers determines the sign of the Seebeck coefficient, hence, α is negative for n-type semiconductors and positive for p-type semiconductors [15].

Secondly, the Peltier coefficient π is defined as the rate of heat flow Q at a junction, to the current across the device I:

$$\pi = \frac{Q}{I}$$  \hspace{1cm} Equation 2-3

Figure 2-4. Set up diagrams for: (a) Seebeck effect, (b) Peltier effect.
2.3 Figure of merit ZT (TE generation and Refrigeration efficiency)

The dimensionless figure of merit $ZT$ is a measure of the performance of a thermoelectric material where the higher the $ZT$, the higher the overall efficiency of the device, thus, a higher output power. It is defined as:

$$ZT = \frac{\alpha^2 \sigma}{\kappa} T$$  \hspace{1cm} (Equation 2-4)

Where $\sigma$ is the electrical conductivity, $\kappa$ the thermal conductivity and $T$ is the average temperature at which the device is measured at.

Thermoelectric materials can be used as power conversion devices when a temperature gradient induces a Seebeck effect and as refrigerators when current is flowing through a junction releasing heat in one junction and cold in another. However, the efficiency of a TE generator $\eta_{\text{max}}$ and a refrigerator $\phi_{\text{max}}$ is required in order to assess its performance. First, it is necessary to consider a TE device which includes both p-type and n-type semiconductors sandwiched between a heat source and a heat sink for both generators and refrigerators as shown in Figure 2-5.

![Figure 2-5. Schematic diagrams for, (a) thermoelectric generator, (b) thermoelectric refrigerator](image)
Additionally, before going through the derivation of the equations, let’s identify the different parameters, as seen in the table below:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \phi )</td>
<td>Generator efficiency</td>
</tr>
<tr>
<td>COP</td>
<td>coefficient of performance</td>
</tr>
<tr>
<td>I</td>
<td>Current</td>
</tr>
<tr>
<td>R</td>
<td>Material’s resistance</td>
</tr>
<tr>
<td>( T_H )</td>
<td>Heat source temperature</td>
</tr>
<tr>
<td>( T_C )</td>
<td>Heat sink temperature</td>
</tr>
<tr>
<td>( \bar{T} )</td>
<td>Arithmetic temperature</td>
</tr>
<tr>
<td>( \kappa )</td>
<td>Thermal conductance</td>
</tr>
<tr>
<td>Z</td>
<td>Figure of merit</td>
</tr>
<tr>
<td>( \eta_C )</td>
<td>Carnot cycle</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>ZT factor</td>
</tr>
<tr>
<td>( \alpha_{ab} )</td>
<td>Seebeck coefficient</td>
</tr>
<tr>
<td>( \Delta T )</td>
<td>Temperature difference</td>
</tr>
<tr>
<td>P</td>
<td>Input power</td>
</tr>
</tbody>
</table>

**Table 2-1. Equation parameters and their definition.**

For thermoelectric generation:

Since a TE converter is a heat engine, we first need to consider the converter as an ideal generator during operation in which there are no heat losses by convection and conduction through the surrounding medium as well as thermal radiation. Therefore, the efficiency is defined as the ratio of the power delivered to an external load to the heat absorption at the junction between two dissimilar materials a and b:

\[ \phi = \frac{\text{electrical power supplied to the load}}{\text{heat energy absorbed at the hot junction}} \]  

*Equation 2-5*
Assuming that the Seebeck coefficient, electrical conductivity and thermal conductivity are constant and the contact resistances are negligible, then the efficiency can be expressed as:

\[
\phi = \frac{i^2 R}{\alpha_{ab} l T_H - \kappa (T_H - T_C) - \frac{1}{2} I^2 R}
\]

Equation 2-6

Efficiency is a function of the ratio of the load resistance to the sum of the thermoelectric elements (arms) resistances, and at maximum output power, it is expressed as [16]:

\[
\phi_p = \frac{T_H - T_C}{\frac{T_H}{2} + \frac{T_C}{2} + \frac{1}{Z}}
\]

Equation 2-7

Thus, the maximum efficiency is:

\[
\phi_{\text{max}} = \eta_C \gamma
\]

Equation 2-8

Where:

\[
\eta_C = \frac{T_H - T_C}{T_H}
\]

Equation 2-9

and

\[
\gamma = \left(\frac{\sqrt{1 + Z T} - 1}{\sqrt{1 + Z T} + T_h / T_c}\right)
\]

Equation 2-10

Where the arithmetic temperature \( T \) is given by:

\[
\bar{T} = \frac{T_H + T_C}{2}
\]

Equation 2-11

Therefore, the maximum TE generator efficiency is given by:

\[
\eta_{\text{max}} = \left(\frac{T_h - T_c}{T_h}\right) \left(\frac{\sqrt{1 + Z T} - 1}{\sqrt{1 + Z T} + T_h / T_c}\right)
\]

Equation 2-12

The Carnot engine is an ideal thermodynamic generator which takes energy from a hot source and converts some to energy and some is transferred to a cold source, reversibly, with no losses, for which we can defined an 'ideal' Carnot efficiency. For a TE generator, the first ratio of Equation 2-12 represents the Carnot efficiency (ideal heat engine, whose theoretical maximum efficiency can be obtained when the heat engine is operating between two
temperatures) which is a maximum of \(1 - \frac{T_C}{T_H}\); this is, for example, an engine operating between 303 and 773 K results in a 61% Carnot efficiency. Therefore, the Carnot efficiency is the limiting factor for obtaining a high performance TE generator [1]; in practice, generators have a much lower efficiency [3]. To maximise the thermoelectric generator efficiency, it is necessary to obtain a high ZT factor. Also, ideally the generator would run at a high temperature difference, as shown in Figure 2-6. This demonstrates that for a cold junction temperature of 300 K, the generator efficiency increases when there is a large temperature difference combined with a high Z value [15][16].

![Figure 2-6. Efficiency of a TE generator for different ZT values [15].](image)

**For thermoelectric refrigeration:**

Any refrigerator is characterised and expressed by its coefficient of performance (COP). This is obtained by the ratio of the cooling power to the rate at which electrical energy is delivered. So, if there are no heat losses and electrical resistances, the COP would reach the ideal scenario of that of a Carnot cycle. For TE refrigeration, the COP can be greater than unity because the Carnot cycle is given by:

\[
\eta_C = \frac{T_C}{T_H - T_C}
\]

Equation 2-13
Using the Kelvin relationship which relates the Peltier effect and the Seebeck effect at the junction, it is given by:

\[ \alpha_{ab} = \frac{\pi_{ab}}{T_C} \]  

Equation 2-14

\[ \pi_{ab}I = \alpha_{ab} \left( \bar{T} - \frac{\Delta T}{2} \right) I \]  

Equation 2-15

The rate of absorption of heat from the source is expressed by:

\[ Q_{ab} = \alpha_{ab} T_C I - \frac{1}{2} I^2 R - K(T_H - T_C) \]  

Equation 2-16

With the input power given by:

\[ P = \alpha_{ab} \Delta T I + I^2 R \]  

Equation 2-17

So, a refrigerator energy efficiency which is measured by its COP which is defined as:

\[ COP = \frac{\text{Heat absorbed}}{\text{Input power}} \]  

Equation 2-18

\[ COP = \frac{\alpha_{ab} T_C I - \frac{1}{2} I^2 R - K(T_H - T_C)}{\alpha_{ab} \Delta T I + I^2 R} \]  

Equation 2-19

Then, the two current values of special interest are \( I_\phi \) which gives the maximum cooling power and satisfies the maximum COP condition can be expressed as follow [16]:

\[ I_\phi = \frac{\alpha_{ab} (T_H - T_C)}{\sqrt{R(1 + ZT)} - 1} \]

Therefore, the maximum TE refrigerator efficiency is given by [17]:

\[ \Phi_{\text{max}} = \left( \frac{T_C}{T_H - T_C} \right) \left( \frac{\sqrt{1 + ZT} - T_H/T_C}{\sqrt{1 + ZT} + 1} \right) \]  

Equation 2-20
2.4 Solid state materials: Metals, semiconductors and insulators

After describing the efficiency of a TE device and its temperature dependency, it is now important to understand the effect of the electrons and holes. Charge carrier concentration influences the electrical conductivity of a material. The three parameters relevant to thermoelectricity $\alpha$, $\kappa$ and $\sigma$ in (Equation 2-4) are plotted as a function of electrons and holes concentration [16] as shown in Figure 2-7. It demonstrates how the charge carrier concentration influences the ZT parameter. The figure shows that the electrical conductivity increases with increasing carrier concentration while at the same time, the Seebeck coefficient decreases. This leads to an optimum power factor, which is only reached with semiconducting materials due to their ideal carrier concentration, which is of the order of $10^{19} \text{cm}^{-3}$. In other words, semiconductors offer the best compromise between the Seebeck coefficient, electrical conductivity and thermal conductivity which will maximise the efficiency ZT of TE devices. It is noted that although the Seebeck coefficient may peak for a particular doping level, this may not coincide with peak ZT parameter, since the doping level affects also the thermal and electrical conductivities (higher levels increase these). These are taken into account only for the ZT value, not the Seebeck coefficient.

Furthermore, it is known that for most electrical conductors the transport of heat (thermal conductivity, $\kappa$) is performed also by the drift of charge carriers (both electrons and holes) whilst phonon heat transfer accounts for a more significant contribution to the thermal conductivity of nearly $2/3$. From Figure 2-7, it is observed that the electronic contribution (representing $1/3$ of the total heat conducted) increases as a function of the carrier concentration. This further emphasizes that the optimum ZT value can be obtained with a semiconductor material with intermediate values of carrier densities which is located at the crossover between a metal and a semiconductor [18]. This is attributed to a large effective mass (high Seebeck coefficient) but a low carrier mobility (low electrical conductivity); this balance between the electrical parameters can be beneficial since a low electrical conductivity means a low thermal conductivity, thus, a larger temperature gradient across the material is maintained. In addition, semiconductors can be heavily doped with carrier densities ranging from $10^{19}$ to $10^{21} \text{cm}^{-3}$ which would allow a higher ZT value to be obtained. This point can be further emphasized by observing the high Seebeck coefficient and the low electrical conductivity at low carrier concentration. It is noticed that an extremely high
Seebeck coefficient is only possible at low carrier concentrations whereas, a high electrical conductivity is obtained at high carrier concentrations. Therefore, it can be concluded that the Seebeck coefficient is directly proportional to the inverse of the electrical conductivity.

As for thermal conductivity, a material’s properties can be tuned in a way to allow a high power factor and a low heat transfer. This can be achieved by introducing metal alloys that would contain a lattice of atoms with different sizes which would reduce the heat flux while at the same time maintaining electron transport.

*Figure 2-7. Dependence on of electrical conductivity, Seebeck coefficient and power factor on concentration of free carriers [16].*
2.5 Fermi level

In crystalline metals and semiconductors, the transport of charge and heat takes place by carrier drift and carrier diffusion. The thermal vibrations of the atoms in the crystal known as phonons, also carry heat [1]. However, for materials with a high density of free charge carriers, contributions from electronic effects are significantly stronger than those from phonon wave propagation.

Drude and Lorentz proposed the idea of electrical conduction by electrons. But this was not fully understood until the idea of the electrons interacting with the periodic potential in a crystal lattice was introduced. This interaction causes the electrons energy to lie in discrete bands separated by an energy gap [1].

To further understand the transport properties in a solid, it is vital to comprehend the Fermi level. The Fermi distribution function given by equation 2-21 describes the distribution of Fermions (such as electrons) over states of energy (E) in a system.

\[
f(E) = \frac{1}{[e^{\frac{E-E_F}{kT}}]+1}
\]

Equation 2-21

Where:

\(k_B\) is Boltzmann’s constant

\(T\) is the absolute temperature

\(E\) is the energy of the single-particle state \(i\)

\(E_F\) is the total chemical potential

The value of \(E_F\) is the energy of the electron in the highest energy level. When \((E-E_F) >> kT\), the Fermi distribution function equals zero, and when \((E-E_F) << kT\) the Fermi distribution function equals to unity [1]. Figure 2-8 shows the transition of an electron from unity to zero which happens over a range of energies [1]. For an energy between \(E\) and \(E+dE\) which is represented by \(g(E)\), the total number of electrons for an interval between infinity and zero is:

\[
n = \int_{0}^{\infty} f_0(E)g(E)dE
\]

Equation 2-22
Figure 2-8. Fermi distribution function plotted against \( \frac{E-E_F}{kT} \) [1].

When electrons in a conduction band can drift from one energy level (state) to a conduction band. If an empty band for which there are no electrons occupying it or a band that is completely full due to the unavailability of states into which electrons can move into, conduction cannot occur. So, conduction is entirely dependent on those electrons whose energy is such that the states are partially filled. Figure 2-9 shows the different energy bands separated by the energy gap [1]. Another quantity to know, is the density of states which describes the number of states available at each energy level. It is given by the following expression:

\[
g(E)dE = \frac{4\pi(2m^*)^{3/2}dE}{h^3}
\]

Equation 2-23

Where:

- \( m^* \) is the effective mass
- \( h \) is Planck’s constant

Figure 2-9. Energy band diagram showing the valence and conduction bands separated by the Fermi level.
To determine whether the type of solid is a metal, insulator or a semiconductor, it is imperative to know where the Fermi level lies within the energy bands. Thus, a material is called a metal if the Fermi level is located within the conduction band enabling a number of electrons to lie near the vacated states making the solid highly conductive that is, a metal [1][19].

On the other hand, if there is a large gap between the valance band and the conduction band, and the Fermi level is lying within the energy gap, this causes no electrons to drift to the conduction band, the material will be considered an insulator. If the energy gap is small, that is, the Fermi level being near to the conduction band edge, few electrons will make the transition contributing to the conduction process, however, the conduction will be small enough for the solid to be categorised as a semiconductor [1][19][20].

In addition, electrical conduction can be due to positively charged holes which are vacancies that were created due to the electrons making the transition. If there are no majority carriers, then the solid is regarded as an intrinsic semiconductor (undoped semiconductor). Adding impurities (acceptor or donor) to a semiconductor is known as an extrinsic property where the Fermi level is close to the conduction or valence band edges. Figure 2-10 shows energy diagram for different materials [1][20].

![Figure 2-10](image.png)

*Figure 2-10. Schematic diagram of energy states for different solids: (a) insulator, (b) intrinsic semiconductor, (c) n-type semiconductor, (d) p-type semiconductor.*
2.6 Inorganic thermoelectric materials

2.6.1 Bismuth Telluride (Bi$_2$Te$_3$) and other materials

Bismuth Telluride is a commonly used thermoelectric material which first appeared in 1954 [21]. Bi$_2$Te$_3$ has a hexagonal lattice, where atoms of bismuth (Bi) and tellurium (Te) forms separate layers giving rise to a hexagonal lattice shape [15] [22]. The layers alternate and are arranged following the sequence:

$$\text{Te}^{[1]} - \text{Bi} - \text{Te}^{[2]} - \text{Bi} - \text{Te}^{[1]} -$$

These layers are perpendicular to the c-axis, in addition to two a-axis inclined at 60° from each other. Therefore, the properties of Bi$_2$Te$_3$ are anisotropic due to the presence of a layered structure [23]. The Te$^{[1]}$–Te$^{[1]}$ bond is of Van der Waal's type and the bonding between Te and Bi atoms is of ionic-covalent type [24]. The crystallographic structure of Bismuth Telluride is illustrated in Figure 2-11. It is shown that each atom in Bi$_2$Te$_3$ has three neighbours either in the upper or the bottom plane [22][24].

![Figure 2-11. Crystallographic structure of Bi$_2$Te$_3$ by the stacking of cubes along the [111] direction [22].](image)
In the early 1950s, the first experiments on Bi$_2$Te$_3$ have shown that it has a relatively low melting point of 585 °C with a low lattice conductivity [25]. There was an excess of Bi atoms which corresponded to Te vacancies at some sites [21]. This excess seemed to act as acceptor impurities leading to an excess of holes, giving it therefore p-type semiconductor characteristics. It was reported that the Seebeck coefficient was equal to 220 µV/K and an electrical conductivity of $4.0 \times 10^4 \, \Omega^{-1}\text{m}^{-1}$ and a thermal conductivity of 2.1 W/mK. Thus, the calculated Z was no greater than $0.9 \times 10^{-3} \, \text{K}^{-1}$. However, it was still not possible to complete the thermocouple because of the lack of n-type doped Bi$_2$Te$_3$ [1] [24].

By 1955, n-type was obtained by adding iodine as a donor impurity, which meant that a thermocouple was made possible. Z was no greater than $1.2 \times 10^{-3} \, \text{K}^{-1}$ with ZT equal to 0.35. Both conductivity types of doped Bi$_2$Te$_3$ were improved in terms of uniformity, leading to optimised properties such as an electrical conductivity of $4.0 \times 10^5 \, \Omega^{-1}\text{m}^{-1}$ and a ZT of about 0.6 [1].

Bismuth Telluride is marked by the anisotropic mechanical properties, making the electrical and thermal conductivities differ from each other when parallel or perpendicular to the c-axis. Taking into account the thermal conductivity, it is demonstrated that along the a-axis, the value of the lattice conductivity is greater than that along the c-axis by a factor of 2.1 [1][22]. Thus, the direction of choice along the stacked layers would be the c-axis direction for thermoelectric applications [22].

Table 2-2 shows the properties of different compounds and solid solutions of bismuth and selenium tellurides and their alloys, including their TE values (figure of merit parameters) at a temperature of 300 K and their electronic properties (carrier concentration and carrier mobility), in addition to their thermal conductivities.

It can be observed that there is a strong anisotropic behaviour of the electrical and thermal conductivities which means that electrical conductivity is higher in the perpendicular direction whereas heat transfer is lower in the perpendicular direction due to the Van der Waal interactions between the Te$_1$ - Te$_2$ interface. ZT is seen to have a higher value when $Z_{11}$ (response along the a-axis) is parallel to the planes along the stacked layers rather than the perpendicular direction to $Z_{33}$ (response in the c-axis), the only exception is for Sb$_2$Te$_3$ [22]. The Sb$_2$Te$_3$ compound can be seen to have a higher carrier concentration, which leads to a lower Seebeck coefficient and a higher thermal conductivity, especially along the a-axis (in plane). Therefore, it is considered unsuitable as a thermoelectric material. An alternative
route would be to synthesise a ternary solid solution such as Bi$_9$Sb$_{31}$Te$_{60}$ which has a lower carrier concentration and a value of Z as high as $3.2 \times 10^{-3} \, \text{K}^{-1}$ [22].

**Table 2-2. Experimental results on bulk materials and their properties [22].**

<table>
<thead>
<tr>
<th>Column</th>
<th>n-p</th>
<th>T (°C)</th>
<th>$C_p$ ($10^9$ cm$^3$)</th>
<th>$\rho$ (µΩm)</th>
<th>$\mu_H$ (cm$^2$ v$^{-1}$ sec$^{-1}$)</th>
<th>$\alpha$ (µVK$^{-1}$)</th>
<th>$\kappa$ (W m$^{-1}$ K$^{-1}$)</th>
<th>$Z$ ($10^{-3}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$Te$_3$/n</td>
<td>n</td>
<td>582</td>
<td>2.3</td>
<td>10</td>
<td>212</td>
<td>240</td>
<td>2.0</td>
<td>2.9</td>
</tr>
<tr>
<td>Sb$_2$Te$_3$/p</td>
<td>p</td>
<td>575</td>
<td>21</td>
<td>3.2</td>
<td>244</td>
<td>92</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Sb$_2$Te$_3$/p</td>
<td>p</td>
<td>605</td>
<td>10</td>
<td>1.9</td>
<td>313</td>
<td>83</td>
<td>5.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Bi$<em>6$Sb$</em>{32}$Te$_{60}$</td>
<td>p</td>
<td>540</td>
<td>4.8</td>
<td>10</td>
<td>176</td>
<td>194</td>
<td>1.3</td>
<td>3.0</td>
</tr>
<tr>
<td>Bi$<em>{10}$Sb$</em>{30}$Te$_{60}$</td>
<td>p</td>
<td>540</td>
<td>3.5</td>
<td>13</td>
<td>177</td>
<td>225</td>
<td>1.4</td>
<td>2.9</td>
</tr>
<tr>
<td>Bi$<em>{15}$Sb$</em>{31}$Te$_{60}$</td>
<td>p</td>
<td>530</td>
<td>3.9</td>
<td>8.89</td>
<td>190</td>
<td>206</td>
<td>1.5</td>
<td>3.2</td>
</tr>
<tr>
<td>Bi$<em>{40}$Sb$</em>{57}$Te$_3$</td>
<td>n</td>
<td>580</td>
<td>4.0</td>
<td>11</td>
<td>140</td>
<td>223</td>
<td>1.6</td>
<td>2.8</td>
</tr>
<tr>
<td>Bi$<em>{40}$Sb$</em>{58.5}$Te$_{1.5}$</td>
<td>n</td>
<td>580</td>
<td>4.3</td>
<td>11</td>
<td>150</td>
<td>230</td>
<td>1.7</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Column n-p: semiconductor type; T (°C) is the maximum temperature before saturation; $C_p$ is the concentration of charge carriers; $\alpha$ is the Seebeck coefficient; $\kappa$ is the lattice thermal conductivity; $Z$ is the figure of merit.

Figure 2-12 illustrates the state of the art bulk materials and their ZT values in relation to their optimum temperature difference. It is noticed that each bulk material has an optimal maximum operating temperature. For example, Bi$_2$Te$_3$ reaches a ZT peak value at $\sim 360$ K. Since the ZT properties of a material have a strong dependence on temperature, it can be observed from that as the temperature difference increases, the material’s ZT goes up then decreases until reaching an optimum temperature which is due to high temperatures negatively influencing the ZT parameters.

Furthermore, different materials would have different optimum ZT values at various temperature gradients; this means that there is not just one perfect TE material. So, it is crucial to identify the temperature range of the application before choosing the ideal material. For instance, Bi$_2$Te$_3$ would be best for solar absorbers or heat sensors not exceeding temperature gradients of 300 K. However, for exhaust manifolds which have a temperature range from 450 to 800 K, materials like PbTe (Lead telluride) or CoSb$_3$ (Cobalt antimony) would be best suited for this kind of application. As for much higher temperature such as jet engine exhausts, Si$_{0.80}$Ge$_{0.20}$ would be the ideal choice.
CNTs, which have a thermal degradation point of around 500 °C, mixed with surfactants with a thermal evaporation of ~ 362 °C (for Triton X-405) would be potential candidates for thermoelectric power generation for relatively high temperature applications.

After giving a description on the theoretical aspect of bulk materials, specifically Bi₂Te₃, other materials will now be explored. The Dresselhaus group has reported various theoretical predictions for high ZT values for low dimensional materials [26][27]. There were also other research institutions that demonstrated experimentally a ZT value ranging from 2 - 2.5 for low-dimensional structures as well as a superlattices such as Bi₂Te₃/Sb₂Te₃ and quantum dots like PbTe/PbSnSeTe [26][27][28]. Zhao et al [29] have reported the highest experimental ZT for Tin Selenide (SnSe) bulk material, with a value of 2.62 at 923 K along the b-axis and 2.3 along the c-axis and 0.3 along the a-direction. However, this 3-dimensional thermoelectric material is not practical.
for large scale commercial application because of the fabrication process which involves heating at an excess of 1220 K for over 19 hours in several stages [29]. This synthesis process is prohibitively expensive for large scale applications.

2.7 Organic thermoelectric materials

2.7.1 Introduction to carbon nanotubes

From 1960 to 1990, ZT showed a very slow increase in its value for Bi$_2$Te$_3$, remaining the best and most common commercial material to date with ZT $\approx 1$. In the early 1990s, research was conducted an attempt to develop new thermoelectric materials with a better performance. Therefore, two independent approaches were developed; one consisted of introducing new compounds of bulk material compounds and the other using materials with low-dimensionality [12][30].

The theory of using a low-dimensional system is promising for the enhancement of ZT. The three parameters, $\alpha$, $\sigma$ and $\kappa$ for a three-dimensional crystalline system are interrelated, therefore altering these three variables independently so that ZT is increased can be difficult [30]. However, if the variable of size can be tuned by reducing the dimensionality like reaching the nanometer scale, then a dramatic change to the density of states can occur as shown in Figure 2-13.

![Figure 2-13. Schematic diagram for the density of states in bulk materials in 3D, 2D, 1D and 0D dimensionalities [30].](image-url)
A typical low dimensional carbon based material is carbon nanotube (CNT). CNTs are rolled up sheets of graphene known for their electrical, thermal and mechanical properties. They can be semiconducting single walled carbon nanotubes (s-SWCNTs), metallic single walled carbon nanotubes (m-SWCNTs), double walled carbon nanotubes (DWCNTs) and multi walled carbon nanotubes (MWCNTs).

The main constituent of CNTs is the element “carbon” which is commonly seen in nature and our daily life. The type of bonding between carbon atoms is what makes them intriguing. There are three types of bonds known as $sp$, $sp^2$ and $sp^3$ leads to a variety of inorganic and organic materials. For example, graphite is constructed by $sp^2$. Due to its π-bonded out of plane stacked graphene, it results in a high thermal and electrical conductivity. Whereas diamond which relies on $sp^3$ bonding is based on three-dimensions making it extremely rigid and hard due to σ-bonding.

The tubular structure of CNTs results in strong mechanical properties while the π-bonding makes them high conductive. In addition, its 1-dimensional structure and small diameter makes its electronic and thermal properties tuneable due to quantum effects.

In addition to the above properties, CNTs exhibit a different set of Van Hove singularities (VHS) giving rise to electronic energy transitions due to the geometry of wrapping [13] as shown in Figure 2-14. As a result of the curvature found due to the tubular shape of CNTs, the density of states (defines the number of allowed energy states that the electrons can occupy) forms various singularities in the E-K diagram [31].

In SWCNTs, VHS can be seen in the valence band and conduction band with each energy state given a number according to its appropriate sub band. For example, a photon with an energy equivalent to that of the energy difference between $v_1$ to $c_1$ will result in an optical absorption as a consequence of the excited electron. Thus, transitions between these energy bands will result to sharp peaks in the optical spectra of the CNTs.
Figure 2-14. Schematic diagram highlighting the electronic density of states (DOS) for a semiconducting SWCNT. The sharp peaks represent the Van Hove Singularities (VHS) whereas the arrows show the energy difference between the sub bands [31].

Since the 1990s, CNTs have emerged as a promising material with variety of applications ranging from large scale structures for the automotive industry to nanomaterials in the electronic field (sensors, field emission transistors, etc) [32]. CNTs have some interesting properties such as a high aspect ratio, hardness, and large electrical conductivity, etc [33]. CNTs can have different forms, for example, Figure 2-15 describes a graphene sheet rolled into a cylinder along the (m,n) lattice vector [34][35]. The nanotube properties depend significantly on its chirality. Depending on the tube chirality, CNTs can be either metallic or semiconducting [32]. The chiral vector \( \vec{C}_h \) and the chiral angle \( \theta \) describes the atomic structure of the carbon nanotubes. The chiral vector is described by the following equation:

\[
\vec{C}_h = n \vec{a}_1 + m \vec{a}_2
\]

Equation 2-24

Where \( (n, m) \) are integers that describe the unit vectors \( n \vec{a}_1 \) and \( m \vec{a}_2 \) of the hexagonal lattice.
The formation of the honeycombs and the way they are rolled up defines the properties of the nanotubes [33]. Zig-zag structure corresponds to $\theta = 0^\circ$ and $(n, 0)$, whereas armchair corresponds to $\theta = 30^\circ$ and $(n, n)$. The roll-up vector also determines the nanotubes diameter and it is given by the following equation [35]:

$$d_t = \frac{c_h}{\pi} = \frac{\sqrt{3}a_{cc}(m^2+mn+n^2)^{1/2}}{\pi}$$  \hspace{1cm} \text{Equation 2-25}

Where the nearest-neighbour C-C is $a_{cc} = 1.421 \text{ Å}$ in graphite, and the chiral angle is given by:

$$\theta = \tan^{-1}\left[\frac{\sqrt{3}m}{(m+2n)}\right]$$  \hspace{1cm} \text{Equation 2-26}

![Figure 2-15. (a) Schematic diagram of a plane graphene sheet which is rolled up to form a carbon nanotube. (b) Atomic structure of an armchair. (c) Atomic structure of a zig-zag nanotube [36].](image)

2.7.2 CNT synthesis

Since their discovery more than two decades ago, there have been different techniques for CNT synthesis. Carbon nanotube growth can be achieved using different methods which include three categories: laser-ablation, arc discharge and chemical vapour deposition (CVD).

Laser ablation is one way to synthesise CNTs and was initially developed by Smalley’s group in 1995 [37]. This growth technique uses a high powered laser beam in order to
vaporise a graphite target which is mixed with a catalyst. This method is known for its high yield that can reach as high as 70% resulting in less impurities than the arc-Discharge method [38].

Figure 2-16 shows a typical configuration of a laser-ablation system. In a furnace of 1200 °C, a target is scanned by a neodymium doped yttrium aluminium garnet (Nd:YAG). An inert gas (argon) is used to blow the as-grown CNTs and deposit them on a soot collector. The target used for CNT growth can have various compositions such as: iron (Fe), cobalt (Co), nickel (Ni) and yttrium (Y).

In summary, laser-ablation is a physical technique commonly used in the industry. However, it has a common issue consisting in the presence of impurities which requires a post-treatment, thus, increasing manufacturing cost.

![Figure 2-16. Schematic diagram of the laser ablation method. A graphitic target mixed with a catalyst is hit by a high beam laser resulting in CNTs which are deposited on a collector [39].](image)

On the other hand, the arc discharge method is well-used as an industrial technique [40] first proposed by Iijima et al [41] and Bethune et al [42]. It is commonly used to produce single-walled tubes of high quality in a short time where a high current is applied into a pressurized chamber heated at high temperature. It relies on vaporising graphite which will in turn condensate to form CNTs [43]. Consequently, a catalyst (Fe, Co, Ni, etc) is required for single wall carbon nanotubes (SWCNT) growth but it is not needed for multi wall carbon nanotubes (MWCNTs). A typical setup for the arc-Discharge is shown in Figure 2-17 where a constant current flows through two electrodes (cathode and anode). This results in a resistive
heating which increases the temperature of the moveable electrodes. Therefore, a high operating temperature varying between 4000-6000 K helps in breaking down gas molecules inside the chamber and form a plasma. So even though this method requires temperatures above 1000 °C for CNT synthesis, the final outcome is CNTs with fewer structural defects [40]. Finally, the arc discharge has some disadvantages such as the non-production of vertically aligned CNTs, a high process temperature and impurities such as amorphous carbon [44] in addition to random distribution of the CNTs in the vacuum chamber. As a result, using this method for the production of large scale electronic applications is not ideal.

![Figure 2-17. Schematic for Arc-Discharge setup showing two electrodes where a high current is passed through [45].](image)

Unlike the physical vapour deposition (PVD) techniques mentioned above, chemical vapour deposition (CVD) uses a catalyst for CNT growth; it was first developed by José Yacamán et al in 1993 [46]. This technique is usually called catalytic CVD (CCVD), where a volatile carbon source gas is introduced such as ethylene, benzene or acetylene [47]. In other words, a metallic catalyst deposited on a substrate is heated up, and under the correct reactive gas mixtures (Hydrogen and carbon source) and vacuum pressure, the catalyst begins to give shape to nano-islands as shown in Figure 2-18 (a). Following this step, the carbon gas atoms diffuse around the metallic catalyst islands after a reduction process, known as “annealing”, in order to start the CNT yield under specific conditions as seen in Figure 2-18 (b) – (d) [43].
These sets of conditions occur in a reactor chamber, they include, gas ratios, flow rate, set pressure and set temperature. Selecting the correct parameters is of huge significance in determining the output CNT quality, type, and growth rate, but still presents a challenge in obtaining the desired chirality [48][49].

![Image of CNT growth mechanism in CVD systems]

*Figure 2-18. CNT growth mechanism in CVD systems. It shows the carbon molecules diffusing around the metallic catalyst island which is the precursor of the CNT yield [50].*

Using this growth mechanism would require a CVD system. A typical CVD process is shown in Figure 2-19 where an energy source such as a plasma, or a resistivity heated coil, or infrared lamps is used in a gaseous reactor to break down the carbon molecules [51].

![Image of CVD process schematic]

*Figure 2-19. Schematic diagram for the CVD process for CNT synthesis. A hydrocarbon source interacts with a catalyst inside the reactor chamber with the help of a plasma or a thermal source like infrared lamps. The gases flow is controlled by a pressure gauge [51].*
Finally, another synthesis technique is the fluidized-bed method which was used to grow SWCNTs and DWCNTs successfully by Li et al [52]. This method has been employed by Thomas Swan to grow the DWCNTs used for this project (Chapter 4 and 5). This growth technique uses a floating catalyst whose thermal stability is monitored and controlled during the growth process. The catalysts (iron) are filled in porous ceramic magnesium particles where they are held in a fluidized bed in a quartz tube sealed half way along its length to allow the reactant gases to pass. The gases include methane and argon in a ratio of 1:1. The synthesis temperature ranges between 760 °C and 860 °C at atmospheric pressure. The last stage of this process uses a hydrochloric acid bath followed by demonised water to remove the porous particles.

In conclusion, both synthesis techniques have advantages and disadvantages. For example, PVD (laser ablation and arc discharge) is known to produce high quality CNTs with a better reproducibility, but at high growth temperatures (> 1000 °C) with a low yield with no possible way of obtaining patterns on the substrate such as vertical alignment. Also, in the case of SWCNTs, this tends to produce impurities which are difficult to remove. As for CCVD, this method is known for low temperature growth (< 1000 °C), as a consequence, it produces low quality CNTs [53]. However, it is possible to grow CNTs with a high yield on patterns for large scale applications, as well as obtaining vertically aligned CNTs where certain properties such as low contact resistance at the CNT-CNT junctions can be exploited [47]. On the other hand, in order to obtain large volumes of high quality SWCNTs and DWCNTs at temperatures below 1000 °C, the fluidized bed method is preferred.

2.7.3 CNT Properties

The main properties listed in the literature, especially for SWCNTs, are high aspect ratio, high electrical conductivity and a large Young’s modulus which translates to excellent mechanical properties. These properties are necessary in order to obtain a large ZT value and a robust TE device, therefore a brief explanation on some of these properties is given below.

For a SWCNT, the diameter varies around 0.4 nm. The ability to grow CNTs as tall as few millimetres with a nanoscale diameter, will result in an extremely high aspect ratio, greater
than $10^6$, as previously reported [54]. As a result, when using the CVD growth techniques, vertical alignment coupled with high aspect ratio of the CNTs allows a considerable increase in the CNT surface area. This property is particularly important when considering functionalization since it allows dopants such as surfactants that disperse CNTs to attach their molecules onto a single CNT shell, therefore altering their electronic properties. Additionally, if considering VACNTs for potential TE devices, the high aspect ratio gives the possibility to include a large number of thermoelectric elements (n-type and p-type semiconductors) in very small substrates, resulting in high output current. Carbon nanotubes are able to break the link between electrical and thermal conductivity because they are very good thermal emitters (blackbodies); although heat is transmitted via phonons through the length of the tube, a larger proportion is lost through emission, as is also shown later in Chapter 3 (Section 3.2), where we show that, for a random CNT film, the optimum device length is $\sim 1$ cm. For a vertically-aligned CNT device, this is likely to be higher as we do not have the losses associated with CNT-to-CNT junctions. This length limit was observed almost independently of doping or surfactant, within the resolution of our experiment, which indicates that doping is a secondary thermal effect, whilst it will strongly influence electrical conductivity and can thus improve the ZT of the device. Lastly, the current produced by a TE device made of semiconducting SWCNTs will increase with the number of vertically aligned SWCNTs resulting in a high output power but, as discussed in Section 2.2 (TE design considerations), this will increase the current generated only. So, to also increase the output voltage, parallel n and p pairs of elements are needed.

Due to the CNT nanoscale dimensions, especially SWCNTs, they have emerged as promising materials for electronic applications. Understanding the importance of their electrical properties and because they are considered one dimensional wires, has led to investigating ballistic conduction in CNTs, the extremely high charge carrier mobility ($\sim 10^6$ cm$^2$/V.s) and the large current carrying capacity ($>10^9$ A/cm$^2$) [55][56][57]. Conversely, the presence of structural defects in CNTs will hinder the transport properties of the charge carriers due to a large number of sites (holes within a CNT), however, this can be generally overcome if the appropriate functionalization dopant is introduced where these molecules can bond to the carbon molecules filling the empty sites.

Another property is the high mechanical strength because of a large Young’s modulus measured to be as high as 1 TPa, which is five times greater than steel [58]. In addition, CNTs
are known for their elasticity [59] making them better materials when considering applications where vibrations and varying strains and stress are present, such as automotive applications; the typical semiconductor materials highlighted in Figure 2-12 are brittle and would most likely fail in the highly stressed environment of a functioning car engine or exhaust pipe.

Material stability is another useful property when implementing CNTs as TE devices. In general, CNTs are non-reactive when exposed to different chemical environments and would require extreme chemicals such as acids or oxidising agents to affect the outer structure of the CNTs. Therefore, doping CNTs using the right chemical agents is required in order to guarantee a successful functionalization into p and n type semiconductors. In other words, a doping agent will add or remove charges to a certain degree depending on its concentration, from the CNT atoms.

2.7.4 CNT dispersion/functionalization

One of the most common ways to disperse CNTs in an aqueous solution is by adding a surfactant to the mixture. The dispersion technique in itself can be considered a functionalization process because the CNT structure is modified causing a reduction in the surface tension and an increase in the wettability. The type of surfactants used are non-ionic, cationic and anionic, where they all possess a similar structural concept (hydrophilic and hydrophobic ends). There are two main utilities in functionalizing CNTs, firstly it allows molecules or functional groups to adhere to the CNTs and secondly, it alters the wettability properties of the CNTs. This leads to conclude that there are types of surfactant/CNT interactions defined as non-covalent bonding and covalent bonding.

For non-covalent functionalization, this process uses hydrophobic interaction or Van der Waal forces to allow the surfactant molecules to wrap (cover) around the CNT. As shown in Figure 2-20, this positioning of molecules on the CNT surface can be a uniform layer or a series of semi-micelles, where the hydrophilic part of the molecule is facing outward whereas the hydrophobic component is bonded with the CNT structure. Various surfactants have been investigated in the past, such as Sodium dodecylbenzenesulfonate (SDBS) and Sodium dodecyl sulfate (SDS) which are both anionic surfactants [60][61]. Therefore, the main
advantage for non-covalent functionalization is that the CNTs structure remains intact while at the same time improving their solubility in aqueous solutions.

Figure 2-20. Schematic diagram showing the different mechanisms for the bonding of surfactants on the SWCNT surface: (a) Surfactant micelles encapsulating a SWCNT, (b) shows hemi-micellar absorption on the SWCNT, (c) Random formation/absorption of surfactant molecules on SWCNT [62].

For covalent functionalization, structural defects are purposefully introduced within the CNT honeycombs followed by a chemical attachment of the desired molecules to the empty sites. These defects are only achievable if a strong chemical agent such as high concentrations of sulfuric acid or nitric acid are added to an aqueous solution. An alternative, less invasive method is oxygen plasma functionalisation, where oxygen atoms are grafted onto the CNT structure [63][64].
In addition to ionic surfactants, non-ionic surfactants have also been reported to effectively disperse CNTs such as Polyethylene glycol hexadecyl ether (Brij 58), Polyethylene glycol sorbitan monooleate (Tween 80), Poloxamer (Pluronic F-127) and Polyethylene glycol tert-octylphenyl ether (Triton X-405) which will be used for this project to determine the electrical properties of each one and how they can affect each parameter.

2.7.5 Surfactant selection

Surfactants are differentiated by both the properties of their hydrophilic and hydrophobic groups. In an aqueous solution, the hydrophilic end (tail) of a surfactant which is facing outward can be anionic (negative charge), cationic (positive charge), zwitterionic (positive and negative charge) or non-ionic (no apparent charge). As for the hydrophobic end which adheres to the CNT structure, the majority of the surfactants are made up of a linear chain of hydrocarbons [65]. The hydrocarbon chains can have different structural lengths ranging between C₈ to C₂₀. Since most surfactants are used as detergents, their combined roles include: absorption, change in the surface tension and interfacial tension, formation of micelles in water, wetting of solids, dispersing/aggregation of solids, foaming/defoaming and emulsifying/demulsifying, etc [65]. Therefore, a brief explanation on some of these roles and what is happening between CNTs and surfactant molecules is necessary.

Firstly, Absorption is the initial step of the interaction process between a surfactant and a material. At first glance, a surfactant’s major characteristic is to be at higher concentration at the surface than in the bulk liquid. This behaviour can occur at various interfaces such as liquid/liquid interface, solid/liquid interface, etc. Taking the example of our experimental work, which is an air/water surface, it was noticed that the more surfactant there is to completely cover the top of the water surface, the more the physical and chemical changes that occur at that interface. This can be further explained by understanding the effect of the surface tension where it decreases as a function of an increase in the surfactant concentration up to the point where a monolayer of a surfactant is formed, causing the surface tension to level off as seen in Figure 2-21 below.
When considering surfactants in water, it is important to remember that the dilution of the surfactant at the surface is dependent on its molecular structure. Here, the hydrophilic group is drawn to dissolve in water contrary to the hydrophobic tail. The strong bonding of the water molecules between each other is much more than the hydrocarbon chains of the hydrophobic group, therefore, it is withdrawn from water.

Secondly, another characteristic to remember is micelle formation; this can happen at the air/water surface when there is excess in the concentration of the surfactant which will be absorbed until saturation point is reached allowing it to fall and remain in the bulk of the solution. However, the hydrophobic heads are still repelled by water, as a consequence, they form groups of micelles generally in spherical shapes also referred to as colloidal sized clusters. The hydrocarbon chains that form each individual molecule are facing each other in a circular form as shown in the inlet in Figure 2-21 above. These micelles start to form at a point known as the critical micelle concentration (CMC) where the main influences are solubility and viscosity. For example, SDS solubility is directly proportional up to the level where the Kraft point is reached (the temperature at which micelles are formed) in which case a dramatic rise in solubility is observed.

There are many physical properties that depend on the cluster size of the surfactants particles in a solution which will show sudden changes in their values at the CMC point. These

*Figure 2-21. Graph shows the critical micelle concentration point (CMC) [66].*
properties include: detergency, equivalent conductivity, surface tension, interfacial tension, light scattering and refractive index, etc.

It is thought that the hydrophobic groups of surfactants dissolved in solutions cause distortions to the water structure thereby its free energy increases [67]. This is eliminated by the increase in concentration of surfactant molecules at the surface and the orientation of the hydrophobic ends away from the solvent. On the other hand, one way of reducing the system’s free energy is micellization. However, for polar surfactants (anionic and cationic) and non-polar surfactants (non-ionic that do not have Ethylene Oxide groups), increasing the temperature of the solution tends to decrease the number of aggregated clusters due to the high kinetic energy of the molecules.

Solubility is yet another parameter which is important to the field of surfactants. The best way to increase the solubility of surfactants is to increase the temperature of the aqueous solution.

Lastly, dispersion is also a characteristic used in this project where individual CNTs are separated from each other. When a solid (e.g. CNT) particle is added to a liquid solution like water, its suspension is facilitated by the use of a surfactant which will allow the particles to be stable and spread uniformly within the bulk of the solution. Solids added to a large volume of water will create new interfaces of solid/liquid, as a consequence, the surfactant’s role in this case is to reduce the interfacial energy therefore resulting in the formation of new interfaces [68].

Choosing the ideal surfactant would depend on the type of charge on the hydrophilic group and the type of surface (material) that will interact with it. For example, to make a material’s surface (negatively charged) hydrophobic then a cationic surfactant is ideal. The surface will absorb the surfactant with its positive polar group contained in the hydrophilic head, which is facing towards the surface with negative charge due to electrostatic forces (attraction), whereas the hydrophobic group is oriented away from the surface making it water repellant. However, if the surface is to be characterised as water-wettable (hydrophilic), then cationic surfactants should be avoided [67].

On the other hand, non-ionic which have no apparent ionic charge (neutral) tend to be an all-purpose surfactant since they can absorb onto surfaces with either the hydrophilic or hydrophobic group orientated towards the surface, depending on its charge.
2.8 Optimisation of Thermoelectric properties

2.8.1 Increasing the power factor

The power factor is defined as the product of the Seebeck coefficient squared and the electrical conductivity ($\alpha^2 \sigma$). These two parameters are important since they depend strongly on the charge carriers’ concentration. Therefore, obtaining a high figure of merit requires a high carrier concentration which leads to a high power factor. Increasing the power factor is an active research area that requires a deep investigation of both Seebeck coefficient and electrical conductivity. As shown in Figure 2-7, an increase in the electrical conductivity results to a reduction to the Seebeck coefficient.

An example of increasing the power factor in bulk materials is reported by Li et al [69]. It is believed that incorporating hard Silicon carbide (SiC) nanoparticles into Bi$_2$Te$_3$-based alloys can enhance not only the thermoelectric materials properties but also the device fabrication [70]. It is demonstrated that in Bi$_{0.3}$Sb$_{1.7}$Te$_3$ alloys, a ZT value as high as 1.33 at 373 K was obtained just by introducing an optimised amount of nano-SiC particles. The highest electrical conductivity was reported to be $10.2 \times 10^4$ S/m when adding 0.4 vol% of SiC particles. However, even though the carrier concentration increased from $1.81 \times 10^{19}$ cm$^{-3}$ to $3.39 \times 10^{19}$ cm$^{-3}$, the carrier mobility subsequently decreased from 365.4 cm$^2$ V$^{-1}$ s$^{-1}$ to 212.1 cm$^2$ V$^{-1}$ s$^{-1}$. The addition of SiC particles is understood to cause a reduction in grain size which lead to defect increases, thus, the carrier density increases and the mobility decreases by improving scattering [69]. It has also been revealed that the power factor showed a maximum value of 3.93 mW K$^{-2}$ around 327 when adding SiC particles.

There were also reports of increasing the power factor in SWCNTs. Nonoguchi et al [71] reported 33 organic compounds used as dopants for tuning p-type and n-type SWCNTs for the usage of thermoelectric power conversion materials in a temperature under 400 K. Among all the 33 compounds, 18 of them: (phosphine derivatives and amine-, and imine-containing molecules) have been reported to have successfully switched p-type SWCNT into n-type SWCNTs. A Seebeck coefficient of -72 $\mu$V/K was determined when SWCNT film was doped with triphenylphosphine (tpp) compared to polyethyleneimine (PEI) doped SWCNTs which had a value of -34 $\mu$V/K. The films doped with tpp and dppp
(1,3-bis(diphenylphosphino)propane) show the highest power factor, almost 2.5 times higher than PEI doped SWCNTs with a value of 25 µW/mK². This clearly shows that enhancing the Seebeck coefficient improved the power factors significantly [71][72][73].

2.8.2 Minimising thermal conductivity

A typical way of reducing the thermal conductivity is by scattering of phonons on different types of defects. Defects can scatter the charge carriers and the lattice vibrations. However, electrons and holes have a greater mean free path than phonons therefore carrier mobility is expected to be affected more than on the lattice conductivity. During experiments, it seems that the mobility of the charge carriers to the lattice conductivity can be increased via defect scattering [1][74]. In semiconductors, the study of heat and transport is critical if the issue of a high ZT needs to be tackled. Thus, the knowledge on materials properties is required and how thermal conductivity can be decreased in a selective way is critical.

It is important to take into account that thermal conductivity of a semiconductor includes two components that transport heat: the electronic component \( \kappa_e \) (electrons and holes), the lattice component \( \kappa_l \) (phonons travelling through lattice) [9]. The Widemann-Franz law directly relates the electronic component to the electrical conductivity and it is given by [9]:

\[
\kappa = \kappa_e + \kappa_l \tag{Equation 2-27}
\]

and

\[
\kappa_e = L \sigma T = n e \mu L T \tag{Equation 2-28}
\]

Where \( L \) is the Lorentzian factor \((2.4 \times 10^{-8} \text{ J}^2 \text{K}^{-2} \text{C}^{-2})\), \( \sigma \) is the electrical conductivity, \( T \) is the temperature, \( n \) is the carrier concentration, \( e \) is the electron charge and \( \mu \) is the carrier mobility.

Since the power factor is interrelated with the thermal conductivity, then reducing the latter can decrease the power factor. Semiconducting TE materials are heavily doped when mixed with compounds for the purpose of increasing the electrical conductivity. This will cause electrons and holes in heat transport contribution. The significant presence of the electronic component...
components in a material needs to be taken into consideration when minimizing thermal conductivity [9].

There are many ways to reduce the thermal conductivity of TE materials. For example, by alloy disorder which is a mechanism that scatters phonons to improve the electrical thermal conductivity ratio and has proven to be more effective than electron and holes scattering. Scattering by other phonons, grain boundaries, introducing lattice defects tend to minimize the phonon mean free path [74].

Furthermore, the manipulation of the thermoelectric properties of nanowires through quantum confinement of electrons has shown promising developments in energy conversion materials [75]. It is believed that phonon transport in nanowires can behave differently to bulk semiconductors mainly due to the modification in the confinement where boundary scattering can be much stronger than bulk semiconductors [76].

However, reports on thermal conductivity of bulk materials have shown that its contribution results in a high ZT. This is due to the anisotropic and anharmonic bonding found within the structure that led to a lattice thermal conductivity of $0.23 \pm 0.03 \text{ W m}^{-1}\text{K}^{-1}$ at 973 K in SnSe [29].

Low dimensional structure materials on the other hand show a rather high thermal conductivity but can be substantially reduced by quenching of phonon mode in bundles and excessive heat radiation from the surface of nanotubes as demonstrated by Aliev et al [77]. The thermal conductivity found in MWCNTs grown by CVD method was $600 \pm 100 \text{ W m}^{-1}\text{K}^{-1}$ which is less than the predicted theoretical value for SWCNTs estimated to be $6600 \text{ W m}^{-1}\text{K}^{-1}$ [77][78]. The latter value is due to the decreased phonon scattering in a one-dimensional system as well as the direction of the measurement which is in the longitudinal direction (along the CNT) [13]. It is demonstrated that coupling within the large bundles of MWCNTs and within the inner walls of the MWCNTs would decrease its thermal conductivity to $150 \text{ W m}^{-1}\text{K}^{-1}$. This can suppress the phonon modes, therefore, reducing the heat transport of individual MWCNTs. Sheets of MWCNTs further reduced thermal conductivity to $50 \text{ W m}^{-1}\text{K}^{-1}$ due to the interconnections between the tubes and the sheet imperfections like misalignment [77].
2.9 Applications of thermoelectric materials

Thermoelectric technology is viewed as the perfect solution for capturing heat and converting it directly to useful electricity without environmental impacts. Heat can be one of most abundant sources of energy that can be used for thermoelectric conversion. It is estimated that one-third of the energy produced from oil, coal and gas, is used by humans effectively [79][80]. Therefore, as illustrated in Figure 1-1 in Chapter 1, two-thirds of that remaining energy can be harvested from various sources such as exhaust systems in automobiles, thermal power stations and nuclear power plants, etc [81].

Although there is no agreed limit on a theoretical value for ZT, it is generally thought that progress in ZT values is quite slow and low, however, it is not a reason not to explore possibilities in order to improve and optimise the ZT parameters. In fact, with a ZT of around 1 for most commercial TE materials and depending on temperature differences within a system, TE devices can be compared to other renewable technologies in terms of efficiency including single junction PV cells. In addition, currently over 90% of our energy supply is used as heat source and almost 60% of that energy used is wasted as heat. The key purpose for TE systems is reducing the electricity cost. So, what is more important is $ per W, i.e. most profitable PV companies are not based on the highest efficiency.

Currently, refrigeration is an area that is prevailing in terms of applications of TE devices, such as small and portable refrigerators, cooling automobile seats, temperature regulators of semiconductor lasers, and medical and scientific instruments [82].

For power generation, thermoelectric generators have been relied upon in the space industry where TE systems have been implemented in many space probes by NASA. On the other hand, terrestrial applications are fewer; this includes remote locations along the oil pipelines and powered watches that rely on body heat. A major driving force for applications now is in vehicle waste heat recovery since automobiles present themselves as a waste heat source. Therefore, it is estimated that cars only utilise around 25% of the energy from fuel combustion. About 2/3 of the heat is wasted through both the radiator and exhaust pipe. Among the latter two major heat sources in automobiles, the high temperature difference that arises from the exhaust pipe makes thermoelectrics a more suitable option. All major
automobile manufacturers have invested in thermoelectric program in order to investigate and develop waste heat recovery technology. These programs are motivated by the strict policies on CO$_2$ emission imposed by governments. For example, in April 2009, the European Parliament has set new standards (in emission performance) for new vehicles, reducing CO$_2$ emissions from automobiles [83]. From 2012, it is estimated that a car manufacturer must pay extra tax duty as a premium if their registered vehicles exceed the allowed emission limits.

Another factor which should motivate automotive industries to investing in Research and Development in the sector of thermoelectrics is the ever-increasing price of oil and the growing concern in its future availability. World renowned automobile makers such as BMW, Volvo and General Motors are accelerating their pace in the development of energy-efficient TE devices for heat recovery. It is widely thought that electric vehicles are the most-efficient and environmentally friendly type of vehicles [84]. However, considering that producing electricity in order to charge up an electric car requires natural sources like solar, gas, wind and sea current; it renders this type of vehicles fully dependant on large infrastructures in obtaining the energy needed to charge up the batteries. Therefore, they cannot compete directly with petrol and diesel vehicles [85]. On the other hand, petrol and diesel vehicles will always be a source of pollution. Consequently, to overcome these previous issues, one can combine both systems, better known as hybrids. In recent years, the most efficient way of transportation has been identified as hybrid electric vehicles, although they are not of absolutely zero emission due to the use of fossil fuels [86]. Nonetheless, both hybrid vehicles and fossil fuel vehicles use internal combustion engines (ICE) which is a very good source of waste heat, as shown in Figure 2-22. It is estimated that about 40 % is lost as a form of heat, with temperatures exceeding 500 °C at the exhaust manifold. This makes the use of thermoelectric devices a very attractive option. The focus of research activities has been on improving the operating temperature range and conversion efficiency of TE devices [87][88]. Converting this waste heat can positively impact an engine. For example, TE power generators could contribute greatly in reducing fuel consumption by converting waste heat into electricity, therefore, engine performance, reliability and efficiency could be significantly improved. In addition, TE generators could reduce torque and horsepower losses by eliminating secondary loads from the engine drivetrain which would help to decreasing
engine weight by disposing of certain components [88]. As a result, the full power produced by the motor is directed by the drive shaft, thus improving performance and fuel economy. However, TE power generators integrated onto the exhaust manifold can only function if the ICE is burning fuel and not when the engine is off.

As well as using TE generators as integrated systems for ICES, TE technology could also lead to implementing a reversible, reliable automotive air conditioning system that does not use liquid coolants as refrigerants which raise concerns due to greenhouse gas emissions. This could be integrated in a simpler and easier package making it more efficient to operate especially if the TE devices used are flexible such as CNT films. Consequently, TE coolers come with a disadvantage because they will certainly require more electrical power than current mechanical systems [88].

In conclusion, considerations need to be addressed when using these TE generators after purchasing such technology because it requires assessing the savings that a consumer makes. In other words, the economic benefit needs to outweigh the cost. So before engineering a system, fuel consumption should be used as a reference in order to consider system implementation.

*Figure 2-22. Energy flow in internal combustion engines [4].*
2.9.1 Solar thermal energy generation

Solar thermoelectric generator (STEG) is another application for TE devices. The idea is to use concentrated solar energy to generate heat therefore creating electricity [89]. The efficiency of STEGs is defined by the product of the opto-thermal efficiency and the device efficiency. It was demonstrated experimentally by Kraemer et al [90] that a flat-panel STEG with a high thermal concentration achieved a peak efficiency of 4.6% under strong light arrays of AM1.5G (1 kW m²). The resulting efficiency was 7-8 times higher than the previously reported best value for a flat-panel STEG. A large output voltage requires a large temperature difference between the two ends of a TE module, so instead of using costly systems such as an optical concentrator, a highly solar-absorbing surface such as a blackbody (CNT film) is used. The latter converts solar radiations into heat and with the use of thermal concentrators, heat energy is directed onto the TE elements by means of lateral heat conduction. One advantage of such a highly absorbing material (STEG) is that there is no requirement for a tracking system, which in turn can be a cost effective technology for solar energy conversion into electricity. In addition, it can also be integrated as solar collector tubes for producing hot water; this shows the potential of STEGs for generating electricity and hot water simultaneously. Figure 2-23 below illustrates a schematic of the STEG device. Some of the literature has emphasized on the requirement of a high heat flux to be able to make thermoelectric devices more efficient and viable. While such a system is useful in some other applications, it is not ideal for waste heat, where energy conversion naturally involves lower heat inputs. Therefore, it is believed that a TE device system efficiency will reduce if there is a large mismatch in heat flux which eventually leads to extra drops in temperature differences for TE devices.

Every year, the levelized cost (constant cost per unit of electric power generation), instant cost, output power and overall performance of renewable systems are assessed by the energy commissions which are then compared with alternative technologies in energy conversion [91][92]. Since TE materials are not widely commercialized, they are not considered in these evaluations. This means that it is up to the TE experts to analyse the cost and how it stacks up with TE device performance. It is estimated that the capital cost of the TE elements varies between 2$ - 5$ per Watt, and their life time is between 15 to 20 years, this makes
thermoelectrics in close competitions with other technologies [91]. However, there is a lack of information about the levelized energy cost. Therefore, to consider TE generators for wide scale applications, an accurate evaluation of the cost per unit power is necessary.

![Diagram of a STEG system made with thermoelectric elements](image)

**Figure 2-23. Schematic diagram of a STEG system made with thermoelectric elements (p-type and n-type semiconductors) and flat a panel on top which acts as a solar absorber (thermal concentrator) [90].**

### 2.10 Summary

In this chapter, the theory behind thermoelectricity has been examined by defining the Seebeck and Peltier effects. Assessing a TE device performance was done by analysing the three key parameters of the ZT equation. In addition, an explanation is also given on the optimum carrier concentration for obtaining a high ZT and the reasons that make a semiconductor the ideal type of material for TE devices. This is followed by a description on inorganic TE materials such as Bi$_2$Te$_3$ and their advantages by comparing the ZT parameters of difference alloys. On the other hand, an analysis is done on low-dimensional materials like “CNTs” which is the material used for this project. The physical structure and electronic properties of CNTs are introduced as well as a comparative
analysis on the different synthesis techniques used for growing CNTs. For this project, the PTCVD which is described in Chapter 4 (Section 4.1), is the preferred technique due to its ability to produce vertically aligned CNTs at low temperature growth. Furthermore, the theory on the functionalization and dispersion of the CNTs is explored by assessing the bonding of the hydrophobic tail to the CNT structure and the hydrophilic head groups which face towards water. In addition, a description on the selection of the requirements in selecting surfactants is also provided. Finally, the importance of TE devices is stated by highlighting different applications of TE devices such as hybrid systems and solar absorbers.
3 Characterisation techniques

As discussed in chapter 1, the main objective set for this project is to obtain a high performance lightweight TE device composed of CNTs. This requires characterisation techniques capable of accurately measuring different parameters over many length scales. In this research, various analytical methods were used to probe samples in order to collect and compare data with previous published work in the field of thermoelectrics. This has led to novel directions that were key to achieving the targets set for this research. The theory and experimental set up of the characterisation techniques used will be explained within this Section, as well as the reasons behind why each method was selected for the project success.

3.1 Electrical conductivity measurement

Electrical conductivity is defined as a material’s ability to conduct electric current. It is one of the key components of the ZT parameters. Measuring this accurately can help to understand the behaviour and characteristics of the charge carriers. In addition, Chapter 5 will explain how the electrical conductivity is directly related to the Seebeck coefficient. One of the challenges facing accurate measurements of electrical conductivity is the geometry of the samples (CNT network, CNT rope, etc), which can significantly affect the measured as well as the recorded values. In essence, it has been reported that conductivity values for SWCNT films range from 12.5 S/cm [93] to ~ 10,000 S/cm [94]. Films made of HiPCo SWCNTs dispersed using oleum were reported to have values from 900 - 1300 S/cm [95]. Other groups reported conductivity values for SWCNT films from 200 - 500 S/cm [38][96] [97]. However, for the axial conductivity of a SWCNT rope, as opposed to a film, all reported values of CNT films were well below the range of 10,000 - 30,000 S/cm [98]. Therefore, it is believed that the lower electrical conductivity values reported for SWCNT films are potentially due to the misalignment or bundling of the CNTs, the increased number of Schottky barriers and discontinuous contacts that arise in the form of tube-to-tube junctions, resulting in higher resistances [99]. This inhomogeneity and lack of a consistent organised distribution of the CNTs, cause various complications when measuring the electrical conductivity of a SWCNT film. So, it is important to come up with an appropriate measurement method for CNT films.
In this instance, two methods were used for the conductivity measurements in order to confirm the accuracy of the data; the Van der Pauw technique and the transmission line measurement (TLM) technique. Both methods require the same key sets of conditions to be met in order to be effectively used, such as: uniform shape, homogenous thickness and no porosity. According to Zhou et al [100], it was claimed that a vacuum filtration technique results in homogenous CNT films which meet the required key sets of conditions for the two chosen electrical measurement methods. Therefore, as an identical filtration method was used, it can be suggested that the CNT films in this project should also be suitable for these measurement methods.

Both techniques require the calculation of the sheet resistance ($R_s$) in order to determine the resistivity. The sheet resistance is defined as the resistance between two opposing edges of the square sheet to be measured. The measuring current flows through a cross-Sectional area ($Wt$), where ($W$) is the width and ($t$) is the thickness of the film. The length of the sample is ($L$), therefore, the resistance $R$ is given by the following expression [101]:

$$ R = \rho \frac{L}{A} = \rho \frac{L}{Wt} $$

Equation 3-1

Substituting for $A$ gives:

$$ R_s = \frac{\rho}{t} $$

Equation 3-2

Therefore, the sheet resistance is independent of the length $L$:

$$ R = R_s \frac{L}{W} $$

Equation 3-3

So, the electrical resistivity $\rho$ and electrical conductivity $\sigma$ can be defined as:

$$ \rho = R_s t $$

Equation 3-4

$$ \sigma = \frac{1}{\rho} $$

Equation 3-5

For electrical characterisation, an analysis of examples of sets of data obtained from the CNT films that will be described including their fabrication process in detail in Chapter 5. The data analysis includes the standard deviation and the standard error. The former is defined as a measure used to quantify the number of variations from multiple repeated data
points (measurements), whereas the latter is defined as an estimate of the standard deviation. So, by applying the following formulas, the accuracy of a measurement can be estimated using the equations below:

\[
\text{Standard deviation: } s = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N-1}} \quad \text{Equation 3-6}
\]

\[
\text{Standard error: } e = \frac{s}{\sqrt{N}} \quad \text{Equation 3-7}
\]

3.1.1 The Van der Pauw method

The van der Pauw technique is applicable to thin uniform samples with relatively small Ohmic contacts [102]. This technique was developed by van der Pauw in 1958 as a method to measure the resistivity and Hall coefficient of arbitrary shaped film semiconductors [103]. The van der Pauw technique is widely used in the semiconductor industry for calculating the resistivity of thin films making it a convenient method to use in this project. It involves the use of the any arbitrary thin shape with four small ohmic contacts placed by the four edge corners of the sample. The objective of this measurement is to determine the sheet resistance which will be used to calculate the electrical conductivity as, seen from Equation 3-1 to 3-5.

Schematic explanation of the Van der Pauw technique to determine the sheet resistance of a CNT films is presented in Figure 3-1. Unlike the linear four point probe which provides the resistivity in the direction of the contact points, the Van der Pauw method uses four probes that are placed around the perimeter of a sample, this way, it provides an average value for the resistivity by using the various combinations as seen in Figure 3-1 [103]. In addition, this setup prevents the need for any modification or patterning on the thin film samples surface such as gold evaporation; consequently, it allows further testing on the same samples.
Equations 3-8 below show how these combinations work. The underlying principle consists of feeding current and measuring the voltage drop at the opposite sides. Using a current source with a low internal impedance to one side of the sample as seen in Figure 3-1 (a) between 1 and 2, this allows minimal parasitic current losses. Then, using a high impedance voltmeter to the opposite edge between 4 and 3, it allows the two probes to draw very little current.

The various configurations in Figure 3-1 are obtained by effectively rotating the sample by 90°. This allows us to find resistances $R_A$ (current $I_{14}$, $I_{32}$) and $R_B$ (current $I_{21}$, $I_{43}$) which can be calculated from Equation 3-8, 3-9, 3-10 [105].

\[
\begin{align*}
R_{43,12} &= \frac{V_{43}}{I_{12}} & R_{34,21} &= \frac{V_{34}}{I_{21}} \\
R_{32,41} &= \frac{V_{32}}{I_{41}} & R_{23,14} &= \frac{V_{23}}{I_{14}} \\
R_{12,43} &= \frac{V_{12}}{I_{43}} & R_{21,34} &= \frac{V_{21}}{I_{34}} \\
R_{41,32} &= \frac{V_{41}}{I_{32}} & R_{14,23} &= \frac{V_{14}}{I_{23}}
\end{align*}
\]

Equation 3-8

So, from the two perpendicular directions, the average resistances $A$ and $B$ can be defined as:

\[
R_A = \frac{R_{43,12}+R_{34,21}+R_{12,43}+R_{21,34}}{4} \quad \text{Equation 3-9}
\]

\[
R_B = \frac{R_{32,41}+R_{23,14}+R_{41,32}+R_{14,23}}{4} \quad \text{Equation 3-10}
\]
Therefore, by inverting the Van der Pauw equation, sheet resistance $R_s$ of the CNT sample can be calculated numerically using [105]:

$$e^{-\frac{nR_A}{R_s}} + e^{-\frac{nR_B}{R_s}} = 1$$

**Equation 3-11**

Figure 3-2 below shows the schematic of a sample holder and the four electrical pins (gold plated) located at the four corners of a sample, as well as the experimental setup which displays the pin connectors and the sample’s location.

(a) 

(b)

![Figure 3-2. (a) Schematic diagram for Van der Pauw measurement sample holder, (b) measurement rig where sample is placed on top of the black square holder and the four external pin connectors are used to make good electrical contact [104].]

The electrical measurements using this method were performed at the National Physical Laboratory (NPL) with the collaboration of Dr Christos Melios.
3.1.2 Transmission line measurement

The Van der Pauw technique involved the use of four contacts (two for current and two for voltage). This has allowed us to determine the sheet resistance while maintaining minimal contact resistance; in other words, the parasitic resistances (contact resistance, probe resistance, etc) are negligible due to the low potential difference that arises from very small current [106]. Therefore, it is important to use another method to have an estimation of the contact resistance.

In this situation, the method used is the Transmission Line Measurement (TLM). This technique uses two probes to measure the resistance and subsequently determine the resistivity of the CNT films [107]. It involves the evaporation of contacts on the CNT mats separated by different distances in order to obtain the sheet resistance and resistivity. So, the “Univex eBeam” was used to evaporate gold lines of 80 nm thickness on the CNT film films. The dimensions of the contacts are 1mm in width and separated by 1, 2, 3, 4, 6 and 8 mm.

Figure 3-3 below shows the dimensions of the TLM technique [107]:

![Figure 3-3. Metal contacts configuration for the TLM method, different spacings are used between the metal strips for accurate measurements [107].](image)

After plotting total resistance versus spacing between contact lines as shown in the Figure 3-4 below, the intercept with the y-axis provides the contact resistance $R_C$, and the gradient equals $R_S/W$ gives the sheet resistance $R_S$ [107].
Figure 3-4. Typical graph of resistance showing the TLM method for various contact separations. The data from the graph determines: \( T_L = \text{transfer length} \), \( R_C = \text{contact resistance} \), \( R_S = \text{sheet resistance} \) [107].

A further evidence of the accuracy of this setup is shown by calibrating the measuring rig against a known material such as Palladium as shown in Figure 3-5 below.

Palladium films were deposited using DC-sputtering. It is observed that the resistivity values are different for the palladium samples. The high resistivity of the 9 nm sample (~186 x 10^{-9} Ω·m) is due to the oxidised layer forming upon exposure to oxygen. In addition, thin film fabrication can produce layers with grain boundaries and uneven surfaces which can affect
the electrons’ mean free path [108]. This has resulted in an 86% error as compared to the reported resistivity value for palladium. On the other hand, a thicker sample eliminates this problem by producing a very uniform smooth surface which is less prone to oxidation. Therefore, a more accurate measurement for the 112 nm sample can be achieved which resulted to only 5 % error (~ 105 x 10^-9 Ω.m).

In the case of our CNT film samples, the CNT content chosen for the fabrication process as described in Chapter 4 (Section 4.2.1) resulted in various thicknesses which vary from 23 to 74 µm.

3.2 Seebeck coefficient measurement

In addition to the electrical conductivity, one of the key ZT parameters is the Seebeck coefficient. When a temperature difference exists between the two ends of a thermoelectric module, the motion and diffusion of the charge carriers is affected, therefore a potential difference is obtained; this is the principle of the Seebeck coefficient. This phenomenon occurs when the charge carriers (electrons or holes) start to diffuse due to the hot end having more kinetic energy compared to the cold end. The reverse of this process is known as the Peltier effect, where the diffusion of electrons under an electrical potential leads to a thermal gradient.

To comprehend the measurement principles of the Seebeck coefficient, it is necessary to understand heat transfer. Heat is transferred within a solid material by means of collisions and diffusion of particles within a specimen due to a temperature gradient. Heat is transported via different mechanisms in a material. For example, through the vibrations of atoms in a crystal lattice (phonons) or through the change in a crystalline structure, or via electron transport. So, taking electrons as the majority charge carriers in a conductive material, they can transfer heat from the higher temperature end to the lower temperature one, giving rise to the Seebeck effect. This continuous drift of electrons is stopped by the development of a voltage potential in order to maintain equilibrium, which is quantified by the Seebeck coefficient [109]. This ZT parameter has units of voltage per unit temperature, commonly expressed in microvolts per Kelvin, and is described in Equation 2-1 in Chapter 2 (Section 2.3).
After this brief introduction to the Seebeck theory, a discussion on the measurement setup used for the CNT films is required. Figure 3-7 (a) illustrates an arrangement for Seebeck measurements including the schematic diagram where the temperature differences (ΔT) are measured by K-type thermocouples, and the voltage difference is measured by a voltmeter. However, the actual setup had to be improved radically. The old setup consisted of a sample holder (a copper block where the CNT samples on glass slides can be clamped) and two electrical probes mounted on two magnetic blocks; one of these probes is shown in Figure 3-6 (a). This gave the advantage of controlling the probes by lowering them using a knob and placing them on both ends of the sample. These probes had been used initially mainly to prevent any damage to the CNT films since manually handling multimeter probes for example, would risk breaking the film. In addition, the probes were connected to copper wires and required soldering points along the electrical lead, which adds extra electrical and thermal resistances. In addition, making sure that the probes had good electrical contact required pressure to be put on the CNT films which can cause small cracks. However, in some instances the films were electrically connected using silver paste on two parallel copper tapes where the probes could be lowered straight into the tapes as seen in Figure 3-6 (b).

![Figure 3-6](image_url)

*Figure 3-6. (a) Previous electrical probe used for the old setup. The benefit from using it was the ability to lower the probe using the right hand knob. This allows to carefully control the pressure put on the CNT sample, (b) Image showing spring loaded probes manually controlled to prevent damage to the CNT films if they are in direct contact.*
One of the issues to overcome when measuring the Seebeck coefficient is thermal resistance. It is defined as the resistance of a material to the heat flow at the junction between the electrical contacts and the samples. In contrast, thermal conductivity is a material’s property which describes its ability to conduct heat. Thermal conductance is comparable to electrical resistance. The latter is the potential difference between two points divided by the current flowing across them. Thus, it can be concluded that there are similarities between voltage and temperature and current and heat transfer. In essence, a voltage difference is generated as a result to electrical conduction, whereas thermal conduction occurs as a consequence of a temperature difference.

Thermal contact stability at the interface between the hot source and the CNT films is key to improving the performance of the TE device. Since most surfaces including the CNT films used are not perfectly smooth, there will be an air gap between the samples and the heat source. Additionally, a thermal contact resistance is generated because of the large difference between the thermal conductivity values of both air and samples which causes a contraction of the heat flow [110]. Therefore, the output power will decrease due to the existence of the thermal resistance which reduces the temperature gradient between the hot and cold side.

It has been reported in a previous study [111] that eliminating air gaps at the interface can be achieved by using thermal grease which contributes to decreasing the contact resistance.

After reviewing all the potential issues that can arise for the Seebeck measurements, various improvements were done in order to obtain near accurate data as seen in the new schematic setup shown in Figure 3-7 (a). First of all, the measurements were performed in vacuum, which can help in reducing thermal losses. For the preparation of the samples, silver epoxy was used at the interface. The kit consists of both the resin (silver paste) and the hardener (cure); the ideal mixture was 1:1 ratio. The curing time was 24 h at 25 °C or 20 - 30 min @ 100 °C. The thermal conductivity value for this material is around 11 W/m.K. In addition to using a highly conductive material to guarantee both thermal and electrical contact a glove box was used in order to prevent oxygen from being trapped at the interface (silver epoxy and CNT film), thus minimising thermal resistance. Also, for each sample measured, the electrodes were soldered onto the copper tapes which will ensure an ohmic contact. Whereas the thermocouples were covered by copper tape to reduce thermal loss.
Figure 3-7. (a) Schematic diagram showing the components used for the Seebeck measurement of the new setup, (b) measurement rig includes a vacuum chamber and multiple crocodile clips to be connected for powering up the platinum resistors, as well as voltage Mueller clips for recording potential differences across the CNT samples, plus thermocouples for temperature recording, (c) example of CNT samples placed on a glass slide for better handling where copper tapes and silver epoxy are used to electrically and thermally connect the CNT samples.
In this project, for ease of handling and due to the fragility of the CNT films, the samples were placed on a glass substrate positioned between two conducting copper tapes as seen in Figure 3-7 (c). Another reason for choosing a glass slide is its low thermal conductivity which is \( \sim 1 \text{ W/mK} \). This makes heat transfer from the hot side to the cold side extremely slow, thus preventing any negative influence on the cold side.

One end of the sample is heated with a platinum resistor (set at a higher voltage) acting as an active heater while the other end which acts as a heat sink was also connected to another platinum resistor (set at lower voltage); this is to create a linear temperature gradient across the film. This renders the CNT sample to go through a drift phase where the charge carriers are thermally excited and drawn to the cold side, followed by a steady state. Therefore, before collecting any data, the system must be in a steady state which takes around 480 seconds making the overall acquisition time to 500 seconds for each temperature difference as seen in Figure 3-8. The linearity is particularly important because the Seebeck coefficient is highly dependent on temperature change; the charge carriers’ diffusion from the hot end to the cold end varies depending on the temperature difference across the CNT films. Therefore, to obtain a constant Seebeck coefficient, the measurements were carried out using the Keysight B2902A where the potential difference was computed across the samples at five temperature gradients within a small range from 7 to 18 °C \( (\Delta T_1 \text{ to } \Delta T_2) \). To reduce the need for recovery time, all measurements were performed from a low temperature difference to a high temperature difference, after reaching steady state. The cold side temperature does increase over this period, reaching a maximum increase of \( \sim 3-4 \text{ °C} \); this is small compared to the highest temperature difference \( (35 - 40 \text{ °C}) \) and more accurate readings would require active cooling, which would make the design much more complex (i.e. by adding a Peltier cooler); as a good linear behaviour was observed at higher temperature differences in Figure 3-9, this was not deemed necessary at this stage. This is only applicable to these CNT films, and another material is likely to require active cooling. On the other hand, Thermocouples were placed on the copper tapes in close proximity to the platinum resistors and were covered with small copper tape. The thermocouples are used to register the temperature differences and were measured using the Pico Data Logger TC-08 which has 8 input channels with a high 20-bit resolution ensuring that the kit can detect near instant temperature changes. In addition, for K-type thermocouples, the TC-08 can maintain a
0.025 °C resolution over a wide temperature range (-250 to +1370 °C) according to its data sheet [112].

![Graph showing temperature differences (ΔT) for p-type Pluronic F127/CNT within a range varying between 7 to 18 °C acquired using the Pico Data Logger TC-08. The steady state is reached after ~ 480 Seconds.]

To further understand the difference between the “Old setup” and the “New setup”, a calibration of both systems was needed to highlight the measurement setbacks that can be encountered. Two materials were chosen for this calibration, nickel (Ni) and n-type silicon (Si). The improved setup is referred to as “New setup” which is shown in Figure 3-7 above. The previous setup which was used as a reference method to make improvements in the measurements is referred to as “Old setup”. Figure 3-9 shows the data obtained for the two setups.
Figure 3-9. Calibration of the Seebeck test rig showing two different setups: the old setup and the new setup. The New system shows an increase and a closer value of the Seebeck coefficient to the reported ones. The gradient is displayed which corresponds to the Seebeck coefficient.

The samples used for these calibrations required some preparation. First, both materials including the copper tapes were cleaned using ethanol to remove any oxidized layers. For both samples, it was necessary to scratch the surface at the points where the electrodes would be connected. For the Old setup, this could not be done, however, for the “New setup”, the electrical probes were connected using Silver epoxy.
The Seebeck coefficient value obtained for the “New setup” for nickel is \(-12.6\, \mu V/K \pm 55n\) in comparison to the much lower value of \(-7.1\, \mu V/K \pm 254n\) for the “Old setup”. The reported Seebeck value for Ni is around \(13\, \mu V\) at room temperature [113]. Therefore, a 3% error is estimated when using the improved setup compared to a 43.6 % error for the “old setup”. For the n-type Si sample, the reported values vary from \(-200\) to \(-400\, \mu V/K\), depending on the temperature difference and the doping [114]. The “New setup” gives a value of \(-252.2\, \mu V/K \pm 2\mu\) compared to \(-71.2\, \mu V/K \pm 254n\).

It can now be concluded that issues such as electrical contact, thermal losses due to air and sample care have been successfully addressed with the “New setup” design. This proves the reliability of our system which can be used for the CNT film characterisation as seen in Chapter 5 (Section 5.1).

One example of these measurements can be seen in one of samples, CNT/SDBS p-type film. As seen in Figure 3-10, the Seebeck coefficient obtained from the gradient of the Seebeck voltage as a function of temperature difference is \(~54.4\, \mu V\), with a standard error of \(\pm7.5E-8\). This low error value shows that the close range of temperature differences used for the Seebeck coefficient value is ideal for this research.

Figure 3-10. Linear gradient for 5 data points displaying the Seebeck voltage as a function of temperature difference across a p-type CNT/SDBS film. The resulting Seebeck coefficient value is \(~54.4\, \mu V\).
After choosing the right experimental setup and estimating the error accessioned with the measurements obtained from it, there is now a need to understand the effect of the length of a sample on the temperature gradient which in turn would affect the Seebeck coefficient as seen in Figure 3-12. For Seebeck measurements, based on the theory, it is assumed that the temperature drop is linear for solids with a crystalline structure (like Silicon). However, this was checked for 3 cm in length p-type CNT films (CNT mass = 18.7 mg) as seen in Figure 3-11 and it was found that it is not linear as seen in Figure 3-12 (a). For all the CNT films, after 1 cm, the temperature gradient drops from ~ 40 °C/cm to around ~ 5 °C/cm. This indicates that CNTs are highly emissive (Radiates) as it will be seen in Appendix A (Section I.V.1). After 1 cm, it can be described that the film acts as a ballast resistance which does not contribute significantly to voltage generation as shown in Figure 3-12 (b). The voltage drop indicates that the charge carriers’ diffusion to the cold end is hindered by the increase in the tube-tube resistance (acts as a resistor) which rises up as a function of distance. This, limits the film dimensions to 1cm which is an advantage because it leads to more compact designs as shown in Figure 5-4 (b) in Chapter 5 (Section 5.2) for the application chosen for our CNT films.

![Figure 3-11. Schematic diagram highlighting the heat transfer as a function of separation between the hot side and the cold side.](image-url)
Figure 3-12. (a) Plot showing absolute temperature for p-type CNT films as a function of separation; the temperature gradient drops from ~ 40 °C/cm to around ~ 5 °C/cm after 1cm. (b) Plot displays Seebeck coefficient values vs separation which shows linear drop for most surfactants indicating that the charge carriers diffusion to the cold end is strongly affected by the length due to the increase in contact resistance between individual tubes.

To further highlight the effect of the temperature drop as a function of separation, let’s take a look at the thermal map of a CNT film taken by an FLIR TG165 thermal camera during the heating process using a resistor as shown in Figure 3-13. The camera size is 186 mm x 55 mm x 94 mm (L x W x H) with an IR resolution of 80 x 60 pixels and a spectral range of 8 – 14 µm. The arrow in Figure 3-13 indicates the start of the CNT film and shows that the temperature drops non-linearly. Note that the temperature here is measured via emissivity, which is why the resistor appear much hotter, although nominally, they are at the same temperature.

Figure 3-13. (a) Thermal imaging of the CNT film illustrates the heat transfer along the sample, (b) temperature profile of the CNT film obtained using ImageJ. The RGB values are converted to grey-scale before a line profile is taken. The arrow indicates the start of the CNT film.
3.3 Scanning Electron Microscopy

To analyse the characteristics of the CNTs within the films, a small cut was made in order to inspect the uniformity of the films and to review the height of individual CNTs. This analysis was performed using scanning electron microscopy (SEM). It is a technique used to measure the height of the vertically aligned CNTs (VACNTs) on a silicon wafer and the thickness of the CNT films. It is a quick and non-destructive imaging method conducted in a vacuum environment [115]. In high vacuum, a better resolution can be obtained due to the low scattering between the electrons beam and the gas atoms. Using a focused beam of electrons from a gun, these electrons are then accelerated through a condenser lens where they are converged using electromagnetic coils. Next, with an objective lens, the beam is focused onto a particular area of a sample. To allow movement in the x and y direction, scan coils present between the condenser and objective lenses use electrostatic fields to direct the beam. Once the incident electron strikes the surface of a sample, an elastic or inelastic scattering occurs resulting in: secondary electron emission, back-scattered electron emission, Auger electron emission and X-ray emission. Secondary electron emission is used for morphology analysis. This secondary electron interacts with the detector resulting in an image where the topography and morphology of the sample can be assessed. An example of a CNT film’s small section is shown below in Figure 3-14 (a).

In this project, the samples were placed on a sample holder positioned at a 90° angle to the viewing direction in order to obtain a visualisation of the uniformity of the film and the CNTs. The sample holder on a metallic stub was covered by carbon tape to keep the sample stable. The chamber is then shut and pumped down to a vacuum of ≤ 1 × 10⁻⁴ mbar. The SEM apparatus used for obtaining images is the FEI Quanta ESEM. The accelerating voltage was varied from 5 kV to 30 kV and a spot size from 3.0 to 4.0 depending on the sample. The increase in the accelerating voltage rises up the incident beam of electrons, resulting in a smaller beam spot which can improve resolution. The images obtained were analysed using “ImageJ” software for assessing the height of VACNTs and thickness of CNT films.
Figure 3-14. SEM micrographs displaying CNT films dispersed using SDS: (a) cross Section area of CNT/SDS film showing a uniform CNT film due to CNTs stacked on each other in a random manner, (b) high magnification (90000x) image of randomly distributed CNTs.

3.4 Raman Spectroscopy

Raman spectroscopy is an integral step in this project, it is one of the main techniques in characterising carbon based materials such as graphene and CNTs [116][117]. Its main advantage arises from being a fast, non-destructive method that requires no further sample preparation. Raman analysis provides information of the quality of the CNTs, their electronic nature (metallic or semiconducting) and the diameter of SWCNTs. Below, a brief explanation will be given on the Raman spectrum of CNTs followed by describing first and second order Raman scattering as well as the radial breathing mode (RBM), D- and G- peaks which relate to the quality, electronic and diameter of CNTs.

During CNT growth, there is always a certain degree of structural defects present that affects the electrical conductivity and mechanical strength of the CNTs [118][119]. Therefore, evaluating the quality of the CNTs before any application is necessary. A typical Raman spectrocope uses a laser to probe the lattice vibrations (phonons) of molecules via inelastic scattering of a monochromatic light that is usually sourced from a laser of known wavelength. When light is scattered from an object, almost all the scattering is defined as Rayleigh scattering (elastic process). However, a small percentage is an inelastic process where the scattered light has a different energy from the incident light. From Figure 3-15, the Rayleigh
and Raman scattering can be observed. More specifically, a laser with a given wavelength used for a Raman spectroscope emits a photon that interacts with an electron; this causes an excitation of the electron from the valence band to the conduction band. The excited electron is then re-radiated as scattered light which is classified as Rayleigh scattering. However, for inelastic scattering, there are two classifications: Stokes (emitting phonon) and anti-Stokes (absorbing phonon) Raman scattering. The former is defined by the excited electron falling to a vibrational level whereas the latter is an electron excited from the vibrational level to the valance band [35]. The scattered light is plotted as a function of the energy downshift of the scattered phonons of light, known as Raman shift. In this project, the Raman spectroscope used for CNT analysis is the Renishaw-micro Raman equipped with 2 lasers, green (514nm) and red (785nm) with a scanning range from 170 cm⁻¹ to 4000 cm⁻¹. A silicon wafer with 521 cm⁻¹ silicon peak was used for calibration purposes. Furthermore, before collecting Raman signals from our CNTs, a calibration process is needed where a silicon wafer with 521 cm⁻¹ silicon peak was used. For a CNT sample to be analysed, it is first placed on a stage, then to assess a particular area, a lens with 50x magnification and a laser power of 0.17 mW was used.

There are various peaks that are displayed as a result of this photon-phonon interaction, as shown in Figure 3-16. Each material has its own specific peak wavelength; by comparing against a library of information available at “Horiba Scientific” for example, materials can be evaluated and assessed by comparing the different peak positions. For a CNT sample, at lower Raman shift, the RBM region (100 cm⁻¹ to 500 cm⁻¹) reveals information on the tube diameter.
and the type of CNTs available [35]. For MWCNTs, due to the interference effect resulting between the inner walls, the intensity of the Raman shift is diminished. However, for SWCNTs in diameter range of 0.7 nm < d_t < 2 nm, narrow peaks can be identified for ranges between 150 cm\(^{-1}\) to 350 cm\(^{-1}\) [35]. Therefore, in the presence of these peaks and the use of Equation 3-12, what kind of CNTs are available can be established.

\[
\omega_{RBM} = \frac{A}{d_t} + B
\]

Equation 3-12

Where \(A\) and \(B\) are parameters determined experimentally which depend on the sample being a bundle of SWCNTs or an isolated SWCNT on oxidized silicon substrate [121][122]. According to Dresselhaus, a typical SWCNT bundle with a tube diameter of \(d_t = 1.5 \pm 0.2\) nm, \(A = 234\) cm\(^{-1}\) nm and \(B = 10\) cm\(^{-1}\).

As for other peaks, firstly there are peaks that are denoted by the “*”; some represent silicon dioxide (SiO\(_2\)) peaks whereas the tall sharp peak represents silicon (Si) at 521 cm\(^{-1}\) which can be used for calibration purposes.

Furthermore, the graphitic peak (G) shows the highest Raman intensity because of the carbon atoms that represent the main constituents of a CNT, it is a first order Raman scattering that is found at around 1581 cm\(^{-1}\) in all graphitic materials where an optical phonon mode is found between two dissimilar carbon atoms A and B [35]. For a SWCNT, the G peak is composed of one G\(^{+}\) peak; this is due to vibrations and vector confinements along the circumferential direction whereas the G\(^{+}\) is associated with vibrations along the CNT axis [123]. On the other hand, a DWCNT is known to show four G peaks: G\(^{+}\) and 3 G\(^{-}\) [124].

As for the evaluation of defects within a CNT, this is represented by the D peak which is a second order Raman scattering found at around 1350 cm\(^{-1}\). This peak is a result of the vibrational mode of a symmetrical expansion of the carbon atom cell [35]. The ratio of the D peak intensity to the G peak intensity is a form of CNT quality assessment (purity) where a lower \(I_D/I_G\) ratio is an indication of the a low defect density [117]. For example, a perfect graphite sheet would have no D peak within the Raman signal.
The M-band, found at around 1750 cm\(^{-1}\) is related to multiple layer CNTs such as DWCNTs and MWCNTs which is defined as a combination of vibrational modes in the second order overtone. Another peak known as the iTOLA is attributed to the combinational modes of the in-plane transverse longitudinal acoustic (L(A) mode and longitudinal optical (LO) mode [125].

Finally, the 2D peak which is the second most intense peak after the G-band. This peak is considered an overtone to the D-band, which is referred to as the G’ in Figure 3-16. This number “2” associated to it is in reference to its double frequency shift of the original D peak.

![Raman Spectra of SWCNTs](image)

Figure 3-16. SWCNT Raman signals displaying various peaks: RBM region for determining CNT diameter, Silicon peak used as a reference point, D peak corresponds to the defective sites within the CNTs, G peak related to the graphitic content of CNTs [35].

The peak discussed above can be found in one of the samples that was measured using our Raman system as shown in Figure 3-17. This particular CNTs were purchased from Sigma Aldrich (product code: 773735) and were characterised for the purpose of comparison with the peaks observed in Figure 3-16. Their high quality can be seen form the I\(_D\)/I\(_G\) ratio which was calcualted to be ~ 0.06. This high purity can be attributed to the high temperature process (> 700 °C) used during the growth which consists of a silica supported catalyst CVD method (CoMoCAT CVD). The resulting CNTs have an average diameter of 0.78 nm with semiconducting composition of approximately 95% according to the data sheet [126].
For Raman characterisation, the CNT sample (powder form) was mixed in distilled water, then drop casted on a glass slide followed by heating on a hot plate at 100 °C in order to evaporate water. The laser used for the characterisation was the green laser ($E_{\text{laser}} = 2.41$ eV).

![Raman spectrum image](image)

**Figure 3-17. Typical Raman signal measured using the Raman Renishaw where all the peaks are in agreement to with the reported Raman signals by Dresselhaus.**

Finally, different lasers can reveal the structural information of SWCNTs (CNT diameters). To understand the theory behind it, let’s look at the Kataura plot. It was developed by H. Kataura in 1999 [127]. The plot describes the relationship between the energy separations as a function of the SWCNT diameters. In theory, this plot is obtained and calculated by using $\gamma_0 = 2.9$ eV and $a_{c-c} = 0.144$ nm, resulting in the Kataura plot which is illustrated in Figure 3-18 [128]. The red and blue points correspond to semiconducting and metallic SWCNTs respectively.

The Kataura plot can be useful in the determination of s-SWCNTs or m-SWCNTs by using different excitation energies in Raman spectroscopy. Our Raman Resnishaw system uses two excitation energies, $E_{\text{laser}} = 2.41$ eV (Green) and $E_{\text{laser}} = 1.58$ eV (red). The SWCNTs that fall in the resonance window of the red laser mainly detects semiconducting SWCNTs with diameters less than $\sim 1.5$ nm 46 48 [129][130]. On the other hand, the green laser resonates mostly with both metallic and semiconducting SWCNTs.
Figure 3.18. A typical Kataura plot displays the relationship between the energy separation and the nanotubes diameter (SWCNTs). The red and blue dots refer to semiconducting and metallic SWCNTs respectively. The red and green lines correspond to the laser energies available for the Raman Renishaw [128][131].

3.5 UV-VIS Spectroscopy

For this project, CNTs are used as thermoelectric elements that can be functionalized into p-type or n-type. However, they can also be used for other applications as solar absorbers. Since CNTs are very dark materials, they can heat up due to sun radiations which creates a temperature difference. Therefore, this optical spectroscopy technique is used for understanding the absorptivity of the VACNT samples that will be characterised in Section 4.3.1. The theory behind this technique is when a light source strikes the surface of a sample, the photons interact with matter causing an electron excitation from the ground state to the excited state.

Figure 3-19 describes the operating system of a typical UV-VIS spectrometer (Carry 5000 was used in this project). When photons generated form a light source, it first passes through a slit to limit the wavelength of light entering the spectrometer, mirrors are used to reflect the
photons to a diffraction grating which will then go through the sample before reaching the detector.

![Diagram of typical spectrometer](image1)

*Figure 3-19. Schematic diagram of typical spectrometer, a light source is passed through a monochromator which splits photons by wavelength, which then goes through the sample and the altered light is monitored by the detector [132].*

For characterising the reflectance, an integrated reflective apparatus was used. Figure 3-20 shows the principle of operation of this type of spectrometer, which describes a light beam passing through a small gap then entering the highly reflective integrating sphere (white surface). This incident light will hit the sample and the surface (VACNTs on silicon) resulting in diffuse reflectance, which will then be collected by the detector that will measure both diffuse and specular reflection as shown in Figure 3-20.

![Diagram of integrating sphere](image2)

*Figure 3-20. Diagram of integrating sphere highlighting diffuse reflectance and all the components used for optically characterising a VACNT sample as seen in Appendix A.*
For the VACNT optical characterisation as seen in Appendix A (Section I.V.1), the reflectance properties are measured using this configuration allowing light to pass through a small gap, where the incident light will strike the VACNTs grown on the samples. The latter sample is placed in front of a highly reflective white surface in order to make sure that any transmitted light that goes through the Silicon in UV-VIS range is reflected back.

3.6 Thermogravimetric Analysis

The CNTs used in this project (wet cake) contain significant water as well as other impurities such as amorphous carbon and catalysts used for their synthesis process. Therefore, Thermogravimetric analysis (TGA) is a technique that requires only few milligrams of a sample to evaluate its thermal properties. It is a measure of a change in a sample’s mass as a function of temperature change in a controlled atmosphere (Air or Nitrogen) [133]. In other words, TGA is used to continually heating up a sample at a constant temperature while measuring its weight at the same time. When the temperature increases, the sample will show thermal degradation, evaporation or oxidation. However, in some situations, a metal has a tendency to oxidise when exposed to high temperatures therefore gaining weight. The measurement output is the sample’s weight (either reduction or gain) plotted against a temperature change.

In this project, CNT wet cake (batch of CNT powder) was used when making the CNT films, this requires TGA to assess the water content and any other residual content such as the catalyst used for the CNT synthesis. It is believed that knowing the temperature at which CNTs oxidise can reveal information on their quality, this is because CNTs which are defective will result in oxygen to attack defects in carbon lattice [134]. In addition, any amorphous carbon present in the CNTs will burn at lower temperatures than the oxidation temperature of CNTs, therefore, TGA becomes an experimental technique to assess the CNT quality. Furthermore, TGA can be used to determine the maximum operating temperature of the surfactants and polymer (PEI) used for the fabrication of the TE devices. This is achieved by looking at the various thermal degradation points (temperatures) which can reveal the water content and the residual left at maximum temperature as seen in Figure 4-15 in Chapter 4 (Section 4.3.3)
The TGA apparatus used to identify the amount of CNTs was TA Q500 TGA at the materials lab, the measurements were performed in the air.

3.7 Summary

In this chapter, various characterisation techniques have been explored which are important for this project in order to assess the different electrical structural properties of the CNT films. Each analytical method has been introduced, highlighting their strengths of proper implementation. For the electrical conductivity measurements, two different methods are used which is necessary to confirm the data acquired from both of them. Furthermore, an improvement of the test setup for Seebeck coefficient measurement is explained showing the difference between the old setup and the new one. In addition, an emphasize on the importance of measuring the Seebeck coefficient as a function of separation which will contribute into choosing the ideal length for the CNT films, thus maximising the output power generated form the TE devices.

For the characterisation of the CNTs morphology, SEM spectroscopy was used which is beneficial in analysing the individual CNTs and estimating the CNT films thicknesses. As for the structural analysis of the CNTs, Raman has been described in detail, where each peak is identified.

Finally, TGA is explored whose main purpose is to assess the amount of CNT content found in the samples provided by Thomas Swan. Additionally, it will also be used for estimating the thermal degradation point of each surfactant and polymer (PEI).
4 CNT films fabrication and characterisation

This chapter outlines the experimental methods used in the fabrication process of the SWCNT films. To determine the power factor, the electrical conductivity and Seebeck coefficient data are analysed, as well as the Raman data. The three sub-Sections of this chapter are: characterisation of the Thomas Swan CNTs (SEM and TEM images of the non-dispersed CNTs, their Raman signal and TGA data followed by the fabrication of SWCNT films and TE devices for each surfactant and the characterisation of the TE devices and their modules (n-type and p-type).

Previous work conducted in the field of TE device fabrication was done by various research groups [14][96]-[101]. For example, Nonoguchi et al [135] investigated 33 organic compounds as dopants for CNTs and measured their Seebeck coefficients and fabricated a TE device using the best dopant. Another project was done by Dr Simon King at the University of Surrey [141] where 7 surfactants were assessed for their feasibility in obtaining highly aligned areas of electrospun CNT film nano-fibre. In this PhD project, the research is based on the same 7 surfactants which are used in fabricating the TE devices.

4.1 Characterisation of Thomas Swan CNTs

CNTs were provided by Thomas Swan and Co. Ltd. Their “Elicarb s-DWCNT” wet cake was synthesised using a fluidized-bed chemical vapour deposition (CVD) method [52]. Iron catalyst are filled in microscopic porous ceramic magnesium particles. After the growth process, the particles are removed using hydrochloric acid followed by a wash in deionized water (DW). According to the specifications (Product number PRO920), the average CNT diameter is 0.9 - 1.7 nm with nanotube purity (Defined in Section 3.4) > 70% (catalyst residue, ash and graphitic nanoparticles as the non-pure components) and ~ 4 µm in length. However, for a more detail analysis and a better understanding of the physical and chemical properties of the CNT wet cake, SEM and TEM imaging were done and Raman characterisation was performed, in addition to TGA analysis. This will then ensure the effective use of these CNTs in the films fabrications by determining the content of CNTs and whether or not there are
semiconducting SWCNTs present, and also by evaluating the maximum operating temperature of the CNTs before thermal degradation occurs (evaporation). The SEM will provide a visual analysis of the morphology of the CNTs. TEM will determine the type of CNTs present (SWCNTs, or DWCNTs) and the wall thickness and any defective site along the CNTs structure. With the Raman analysis, the CNT diameter and CNT quality (D peak intensity) can also be determined from the RBM region and from the D to G ratio respectively. Finally, TGA was used to measure the CNT and residual catalyst content.

4.1.1 SEM analysis

A small sample of the CNTs was obtained by filtering 20 mg of CNTs in Deionised water (DW) with no surfactant followed by a drying process in a desiccator for 2 hours to make sure that there is no residual water within the CNT film. This will minimise any contamination when evacuating the SEM chamber. As seen in Figure 4-1, this has resulted in a weak film, with cracks that can be observed as soon as an attempt to peel off a small sample is done, which is an indication of the weak Van der Waals forces between individual CNTs. A further explanation on the theory of surfactants will be given in Section 4.2 of this chapter.

Figure 4-1. CNT film that has been filtered on a PTFE membrane with no surfactant content showing some cracks on the sample.
In order to observe CNTs in depth, a small Section of the CNT film was cut with a scalpel which caused stretching and exposure of the CNTs, then it was placed on a sample holder positioned at a 90° angle to the viewing direction.

Visually examining the CNTs under SEM microscopy allowed us to get an estimation of the tube length, diameter and any defects present as seen in Figure 4-2. The CNTs were mostly found aligned in bundles held together by Van der Waals forces, with tube lengths of 2-3 µm with no clear indication of defects along the CNTs length. However, as indicated in Figure 4-2 (a), there are some high contrast points, which could either be impurities or iron catalysts, or CNT knots, which would imply defects. These residuals can only be highlighted by high resolution images such as TEM imaging which is shown in the next Section.

Figure 4-2. SEM image of a CNT film with no surfactant content; (a) cross Section area of the CNT film showing CNTs stacked next to each other and the red circles highlighting impurities and/or catalyst particles, (b) Higher magnification of the CNTs showing bundles of CNTs
4.1.2 TEM analysis

Another analysis of the morphology of the CNTs can reveal further characteristics such as length, diameter and number of sidewalls. In this case, TEM was used for its significantly higher resolution compared to the SEM. This has provided a much improved structural insight of the type of CNTs provided by Thomas Swan (SWCNTs and/or DWCNTs). These images were obtained by Dr Vlad Stolojan after sonicating the CNT wet cake in methanol followed by a filtration process on a holey-carbon grid, then heated at 120 °C for 10 minutes in order to evaporate any water content. The TEM used for this analysis was the Hitachi HD-2300A microscope. As seen in Figure 4-3 (a) – (c), the high resolution allowed us to identify the number of walls of the CNTs, identifying both SWCNTs and DWCNTs which is correlated with the RBM data shown in Section 4.1.3. However, there was a significant DWCNT presence with diameters ranging between 2 – 5 nm; these would not be seen in the RBM region of the Raman spectrum as they would appear at wavenumbers below the cut-off filter ~130 cm⁻¹.

The CNTs show the little or no sign of defects along the CNTs outer walls, which is consistent with the SEM observations and the Raman I_D/I_G ratio, confirming the high quality of the CNTs. Furthermore, Figure 4-3 (d) shows that there is no noticeable residues such as the iron catalyst or the ceramic used for the synthesis process. This indicates that the post-growth treatment process which, consisted of acid washing the wet cake allowed for the near complete removal of the residual metals as well as the magnesium particles. This indicates that the high contrast spots in the SEM images in Figure 4-2 (a) are either impurities and/or iron catalysts that have been encapsulated within the CNTs, creating a protective layer around the metal residuals [142]. This resulted in a very low density of metal nanoparticles that have survived the acid wash process and are unlikely to contribute to the electrical or thermal properties of the thermoelectric films.
Figure 4-3. TEM images of Thomas Swan CNTs showing double walled CNTs, (b) (c) zoomed in areas of DWCNTs displaying their diameters, (d) low contrast TEM image which doesn’t indicate any impurities or iron catalyst particles. Reproduced from [141].
4.1.3 Raman analysis

Raman Spectroscopy measurement was conducted on the CNT film described previously in Section 4.1.1. Three Raman spectra were obtained using the red laser ($E_{\text{\text{\text{\text{}}}}\text{\text{\text{\text{}}}laser} = 1.58 \text{ eV, 782 nm}}$) from different spots of the CNT film and the average signal of the three was taken. The resulting spectrum is shown in Figure 4-4.

From an initial analysis of the spectrum, it can be concluded that because of the low background and the tall sharp peaks, this is really high purity CNTs [143]. If a sample has high amorphous carbon content, the signal would be very noisy with a high D peak which would require us to remove the background to better assess the Raman signal, however, in this case, it wasn't deemed necessary. Furthermore, the background is typically fluorescence which is usually seen from amorphous carbon.

![Figure 4-4. Raman spectrum of CNT film acquired from red laser 782 nm shows a typical Thomas Swan CNT sample with a D-G ratio of 0.15 displaying the regions of interest and key peaks.](image-url)
The first region of interest in the spectrum as shown in Figure 4-5 (a) displays the RBM region or the Radial Breathing Mode (120 to 350 cm\(^{-1}\)) which gives an indication of the different CNT diameters depending of their Raman shift. There are four distinct broad peaks in this region either SWCNTs or DWCNTs, therefore by applying Equation 3-5 from Chapter 3 (Section 3.4), the diameter of the CNTs was calculated to be 1.61 nm, 1.2 nm, 1.05 nm and 0.93 nm. For DWCNTs, it is known that the difference between the inner and outer tubes is 0.68 nm according to Li et al [124], therefore, it can be seen that the CNTs with 0.93 nm and 1.61 nm (difference is 0.68 nm) represent the inner and outer wall of a DWCNT.

In addition, the variations in the RBM intensity observed are dependent on the density of states (DOS) available for the optical transitions for a particular type of CNT which includes absorption and emission. For example, by using a tuneable laser, the joint DOS can be studied which would allow the determination of the electronic structure of an isolated CNT at a specific wavenumber (Raman shift). This could be achieved by plotting the resonance intensity as a function of the value of the electronic transition energies (E\(\text{ill}\)) between the valence bands and conduction bands [35] resulting in a resonance profile for a given (n,m) nanotube.

To further assess the quality of the CNTs, we took into consideration the intensity of the D peak and G peak. The ratio of I\(_{D}\)/I\(_{G}\) is 0.13 which is another strong indication that these CNTs are of high quality due to the low number of defect sites within the CNT structure compared to previously reported data [144].

When analysing the graphitic structure of the CNTs, the first and most intense peak is the G peak. According to Dresselhaus [35], SWCNTs feature two peaks within the G peak, the G+ and the G- which are attributed to longitudinal optical (LO) and transverse optical (TO) phonons respectively. However, for DWCNTs, we can observe four peaks, G+ and 3 G- modes [124]. The splits displayed in the G peak can be seen in Figure 4-5 (b). This splitting is related to the propagations of the phonons along the nanotube walls whether it is DWCNTs or SWCNTs which will be described in Section 4.3.2.

The four peaks identified in the G peak indicate a mixture of both DWCNTs and SWCNTs, therefore, by Looking into the G peak frequency shift which is normally located at 1581 cm\(^{-1}\) [143], in this particular case, the G peak is at 1587 cm\(^{-1}\); this confirms that the CNTs are not dispersed (forming bundles) [145]. This is what to expect due to the experimental procedure done for this Section, in other words, there was no surfactant added to the
aqueous CNTs solution which would have prevented individual isolated CNTs from agglomerating where the better the dispersion, the closer to $1581\,\text{cm}^{-1}$ [35] we get, as it will be seen in the Section 4.3.2 below.

Other smaller noticeable peaks can be seen in Figure 4-4, like the M band located at $1743\,\text{cm}^{-1}$ which describes multiple layer graphene, and few layer graphene such as DWCNTs and MWCNTs [146]. In this case, there is a small M peak which suggests a single layer tube [35], consequently, it confirms SWCNT and DWCNT presence. Another proof of DWCNT existence is the iTOLA peak found between $1864\,\text{cm}^{-1}$ to $2000\,\text{cm}^{-1}$, depending on the laser energy (1.58 to 2.71 eV); it is a combination of two phonons, the in-plane transverse optical (iTO) and the longitudinal acoustic (LA) [147].
Figure 4-5. (a) RBM region where each peak is used to identify the different CNT diameters, (b) G peak splitting modelled using a Lorentzian function where the fitted curves show 3 $G^-$ and 1 $G^+$, indicating DWCNT.

4.1.4 TGA analysis of CNTs

The assessment of the CNT quantity within the wet cake using TGA can reveal various information as it is described in Chapter 3 (Section 3.6). The importance of this measurement is because CNT samples can be MWCNTs, DWCNTs and/or SWCNTs and can contain amorphous carbon, catalyst used during the growth process (Iron or cobalt nano-particles) as well as water, therefore it is necessary to estimate the exact weight of pure CNTs. The analysis was performed in air, this is relevant especially when considering that a thermoelectric device can be designed to perform at high temperature in air. Various factors, such as defects within the CNTs structure can directly affect the rate at which the CNTs burn off [148]. For example, it is believed that defects contained along the graphitic structure and the end of raw MWCNTs...
can affect the oxidative thermal stability of the CNTs, so by annealing the MWCNTs, it causes a reduction in defective sites thereby increasing their stability in air [149].

Figure 4-6 demonstrates a TGA analysis in air of around 7 mg of wet cake; the TGA data used in this chapter was acquired by Mrs Violeta Doukova from the Surrey Materials Institute. Within the wet cake, it shows that the sample contained 92.35 weight% of water. After steadily increasing the temperature at a rate of 10 °C/min, the water evaporated completely at ~ 90°C and the CNTs start to oxidise. The fact that water evaporated before the 100 °C temperature mark could be related to the confinement of water in the CNTs. According to Das et al [150], when water enters and diffuses through CNTs, it forms hydrogen-bonded molecular chains. Within the hydrophobic environment of the CNTs, confinement softens the water molecules dynamics resulting in a decrease in the water viscosity [151][152]. In addition, the TGA measurements were conducted in dry air; this is because moisture can affect the evaporation of water molecules by increasing the boiling point. Therefore, it can be assumed that various factors such as the viscosity parameter can contribute in the complete evaporation of water below 100 °C.

Furthermore, it is observed that upon reaching ~ 465°C, the CNTs start to show weight loss due to thermal degradation which is lower than previously reported values ranging between 600 °C and ~ 700 °C [153][154]. As a result, it is deduced that the CNT content of the original wet cake is estimated to be ~ 7% weight fraction (7 mg × 0.07 = 0.49 mg of CNT mass). In addition, a final residual weight of ~ 0.8% (7 mg × 0.008 = 0.056 mg of residual mass) remains which potentially consists of residual iron catalyst. However, it was not possible to determine whether the remaining residual mass is in fact iron catalyst because the material left on the TGA’s platinum sample holder couldn’t be removed safely without causing any damage to the sample pan. Nevertheless, the residue had a reddish-brown colour and given the high temperature, it is likely that all carbon had been consumed which means that the residue is most likely the now-oxidised Fe catalyst.
Figure 4-6. TGA graph obtained from ~ 7 mg of CNTs from a batch produced by Thomas Swan and Co. Ltd, measured in air with 92.35% water content and only ~ 7% CNT weight fraction and ~ 0.8% residual mass.

4.2 p-type and n-type CNT films fabrication

In this Section, a detailed investigation was done on different CNT samples mixed with seven surfactants (Anionic, non-ionic and cationic), as shown in Table 4-1 and Figure 4-7.

The choice of these surfactants is based on previous work conducted at the ATI [141]; the work consisted of investigating CNTs dispersion using the surfactants listed in Table 4-1 and others non-listed ones (Brij 52, Triton X-100), which vary depending on their hydrophilic end polarity. Prior to that work, the literature had shown that there has been extensive work done on SDS in dispersing CNTs in aqueous solution, resulting in successful dispersions making it a reliable surfactant. This has made it broadly available at a research and industrial levels due to its known performance in achieving greater loadings for electrospinning purposes [155][156]. Regardless, there was no data available in quantifying surfactant performances in
a manner that would make a systematic comparison possible other than visual inspection. This has led to investigating the 7 surfactants used in this project in a way that would allow the selection of the ideal surfactants for electrospinning CNT nano-fibres.

To compare the data and to achieve the optimum dispersion efficiency, the ratio of CNT to surfactant was chosen to be 1:10. It was then determined after a novel micro-centrifugal precipitation method (to assess the CNT dispersion effectiveness) and TGA analysis that the non-ionic surfactants: Triton X-405, Tween 80, Brij 58 and Pluronic F-127 were ideal and compatible with Polyethylene oxide (PEO) for electrospinning. On the other hand, the TGA data revealed that they show the least amount of residues remaining after annealing at high temperatures. In terms of dispersion capability, Brij 52 and Triton X-100 showed poor results, however, SDS and SDBS demonstrated to be the best at separating bundles into individual CNTs.

Therefore, after consideration of the data obtained previously, it was decided that for this PhD project, the surfactants listed in Table 4-1 were selected for fabricating thermoelectric devices. So, the surfactants were used to disperse/functionize the CNTs followed by the fabrication of TE devices made of CNT films.

These surfactants have shown to have different effects on the electrical conductivity and Seebeck coefficient as will be discussed in Chapter 5 (Section 5.1). The surfactants listed below have shown a non-covalent type of bonding with the CNT structure; this can be correlated to a G peak wavelength shift obtained by the Raman for each sample as discussed in Section 4.3.2. Furthermore, covalent bonding requires strong chemical treatment such as sulfuric acid or nitric acid to purposefully introduce defects within the CNT honeycomb lattice structure. In addition, the exceptional electronic properties of CNTs are lost due to the disruption of the \( \pi \) system [157]. On the other hand, non-covalent bonding as shown in Figure 2-20 in Chapter 2 (Section 2.7.4), uses amphipathic molecules which contain a hydrophobic end that bonds to the CNT structure while the hydrophilic end is facing outward making the CNTs in the aqueous solution more soluble, therefore less prone to aggregate by forming CNT bundles.
Table 4-1. List of surfactants from three different categories depending on the polarity of their hydrophilic ends: anionic with negative charge, cationic with positive charge and non-ionic with no apparent charge.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Chemical name</th>
<th>Composition</th>
<th>Type</th>
<th>Hydrophilic end polarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDBS</td>
<td>Sodium dodecylbenzenesulfonate</td>
<td>C, H, O, S and Na</td>
<td>Anionic</td>
<td>Negative</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium dodecyl sulfate</td>
<td>C, H, O, S and Na</td>
<td>Anionic</td>
<td>Negative</td>
</tr>
<tr>
<td>Triton X-405</td>
<td>Polyethylene glycol tert-octylphenyl ether</td>
<td>C, H and O</td>
<td>Non-ionic</td>
<td>Neutral</td>
</tr>
<tr>
<td>Tween 80</td>
<td>Polyethylene glycol sorbitan monooleate</td>
<td>C, H and O</td>
<td>Non-ionic</td>
<td>Neutral</td>
</tr>
<tr>
<td>Pluronic F-127</td>
<td>Poloxamer 407</td>
<td>C, H and O</td>
<td>Non-ionic</td>
<td>Neutral</td>
</tr>
<tr>
<td>Brij 58</td>
<td>Polyethylene glycol hexadecyl ether</td>
<td>C, H and O</td>
<td>Non-ionic</td>
<td>Neutral</td>
</tr>
<tr>
<td>ADBAC</td>
<td>Benzalkonium chloride</td>
<td>C, H, N and Cl</td>
<td>Cationic</td>
<td>Positive</td>
</tr>
</tbody>
</table>

![SDBS (Anionic) diagram]

![SDS (Anionic) diagram]

![Triton X-405 (Non-ionic) diagram]

![Tween 80 (Non-ionic) diagram]
Figure 4-7. Chemical structure of the surfactants used in these experiments for dispersing the CNTs; non-ionic surfactants (SDBS and SDS) contain a hydrophobic chain of 10 hydrocarbons (CH₂). Triton X-405 has the shortest hydrocarbon chain among non-ionic surfactants, whereas Tween 80 and Pluronic F-127 have the longest chains and Brij 58 has 14. ADBAC can have long hydrophobic chains depending on “n” value which can range from 8 to 18.

4.2.1 Experimental procedure

The main need for this project is to make semiconducting CNT films. A thermoelectric device requires a p-type and n-type TE elements electrically connected in series and thermally connected in parallel. Firstly, a CNT film is obtained after dispersing the bundled CNTs; the oxygen exposed film shows p-type characteristics. Secondly, PEI inclusion prevents oxygen doping by wrapping around the CNTs making the film an n-type semiconductor. However, it is important to point out that a high PEI content will affect the electrical conductivity and a high surfactant concentration means a thicker coating layer, thereby, reducing the electrical conductivity.

In this investigation, the CNTs provided by Thomas Swan were first placed into Polystyrene square-shaped antistatic weighing boat. From the TGA analysis above, 0.275 g of wet cake equals 18.7 mg of CNTs. This amount of CNTs was then mixed with 0.187 g of surfactant in a beaker filled with 100 ml of distilled water. To allow a direct comparison between each
surfactant, the mixture was 0.1% weight fraction of CNTs and 1% weight fraction of surfactant with a ratio of 1:10 (CNT:Surfactant) which was deemed the ideal ratio as reported by previous groups [60][92][93]. However, in Chapter 3 (Section 3.2), we used the data obtained and compared it with a second batch (thin samples). The thin samples required half the amount of the first batch which amounts to 0.275 g of wet cake (18.7 mg of CNTs). The CNTs were then mixed with 0.187 g of surfactant in a beaker filled with 100 ml of distilled water. Preparing the solution for sonication requires degassing which can be done by bath sonication for 60 minutes that can help in removing any gas or air bubbles in the solution which can interfere in the probe sonication process. The high energy delivered to the solution by the sonicator causes an increase in the temperature, thus, the aqueous solution in the beaker was placed in an ice bath, then the CNTs were dispersed by tip-probe ultra-sonication (tip diameter is 1 cm) for 30 min at 300 W, with 40% amplitude, 1 s pulse ON, 1 s pulse OFF. The difference between non dispersed CNTs and dispersed CNTs can be visually analysed as shown in Figure 4-8. Even though individual CNTs cannot be resolved using optical microscopy, it does allow for the direct characterisation of the degree of dispersion of CNTs on a micro scale. It displays how the CNTs on the left have a clear dropout to the bottom, where they are found still agglomerating and in dense clusters. Whereas the solution on the right shows how the high energy produced by the tip sonication causing the CNT bundles to temporality untangle (separating individual CNTs). This allows the dissolved surfactant (hydrophobic end) to adhere to the outer structure of each CNT, therefore, the CNTs are suspended and the solution appears uniformly dark all across the liquid mixture. It is then clear that the direct dispersion of CNTs in water is impossible without a surfactant.

![Figure 4-8. CNTs were dispersed with and without a surfactant for a visual comparison on how dispersed and non-dispersed CNTs appear after sonication; dispersed CNTs (right), Non Dispersed CNTs (left)](image)
The following experiments are aimed at obtaining p-type and n-type semiconductor CNT films. For p-type CNTs, 50 ml of the CNT aqueous solution was placed in a glass funnel onto a PTFE filter with 0.45µm pore size. Next, the filter was primed with ethanol prior to the filtration process as shown in Figure 4-9; this is followed by turning on the pump which allows the distilled water to go through and fall into the filtering flask. For n-type semiconductor CNT films, the remaining 50 ml CNT solution was mixed with 1 g PEI (37 wt% in H₂O) dissolved in 20 ml DW. Next, the 70 ml solution is heated on a hot plate at 55 °C for 24 hours and stirred at 200 RPM, followed by vacuum filtration. The later took longer to filter out because of the solution containing a polymer (PEI) which causes some blockage of the filter pores. Finally, both CNT films are placed to dry in a desiccator for 4 hours to remove any remaining residual water. For characterization purposes, each CNT film (p-type and n-type) made with the surfactants stated in Table 4-1, were cut into stripes: 14 mm x 2 mm.

Figure 4-9 describes the steps taken to obtain a CNT film, thereby constructing a TE device for generating voltage and power external circuits such as a diode.

In this project, there were many experimental problems, therefore, it is important to discuss and outline some of the issues encountered during this process. Firstly, from Section 4.1.4, we identified whether the CNTs obtained from the supplier contains any water or residue, therefore, using TGA is beneficial so that the correct amount of CNTs is weighed. Secondly, after the sonication process is done for “100 ml + CNT + Surfactant” of solution, this has to be divided into two smaller beakers equally in order to obtain a p-type and n-type (after PEI functionalization) CNT films. To make sure that any residue left at the bottom of the larger beaker is not added to just one small beaker, a vortex mixer is used to mix the solution and get an even and uniform aqueous mixture followed by a weighing of both beakers to confirm even amounts of solutions. Thirdly, when functionalizing one of the small beakers into an n-type semiconductor solution, it is useful to cover the small beaker with aluminium foil and allow only a small hole for the temperature probe controller, this way, preventing the water from evaporating quickly when the solution is stirred and heated up at 55 °C which can vary depending on the viscosity of the surfactant added during the initial mixing process.

Lastly, when filtering the solutions, some CNT/surfactant liquids showed the formation of a “foam” which consists of bubbles of gas that can be eliminated by adding acetone to the bottom of the filtering flask, which stabilises the foam.
Figure 4-9. Experimental procedures for obtaining a CNT film: (a) probe sonicator used to disperse CNTs while allowing surfactant particles to adhere to the CNT outer structure, (b) Hot plate to heat up the beaker and a temperature probe immersed into the solution to accurately obtain the desired 55 °C, (c) a vacuum filter system where the solution is poured into the Buchner funnel to obtain a CNT film, (d) a circular shape CNT film that can be cut into specific dimensions.
4.3 Surfactant/CNT films characterisation

4.3.1 SEM analysis

Raw CNTs in their initial state are entangled, which requires a dispersion process before starting the fabrication process of the TE devices. After vacuum filtration of the aqueous solution, the as-obtained CNT films were exposed to oxygen at room temperature (around 25 °C and a relative humidity of 35% ± 4) to convert them to semiconducting p-type samples [72][160]. Thus, a further doping of the CNT solution using PEI is necessary to prevent oxygen absorption. As reported by previous groups, PEI effectively dopes and functionalizes CNTs into n-type semiconductors [160][161]. However, PEI, as most polymers, is an electrically insulating dopant which alters the CNT-CNT charge transport by increasing the contact resistance; this is mostly due to its large molecular chain causing an increase in the overall thickness of the CNT mats [136]. The SEM images in Figure 4-10 illustrates how CNT/SDBS film appears, the cross-section view in Figure 4-10 (a) shows an excellent uniform continuity of the SWCNT network compared to a thicker CNT/SDBS/PEI film with an even coating. The SEM images can also reveal that PEI acts as a coating layer encapsulating individual CNTs [162], therefore preventing oxygen atoms present in the air from penetrating the SWCNTs resulting in the preservation of the n-type characteristic. The remaining thicknesses of all the CNT films can be seen in Table 4-2.
Figure 4.10. SEM micrographs displaying CNT films dispersed using SDBS: (a) cross section area of CNT/SDBS film showing a uniform network of CNTs stacked on each other in a random manner, (b) image of CNTs from CNT/SDBS film, (c) cross section area of CNT/SDBS/PEI film showing PEI infused CNT film resulting in a thicker film, d) image of CNTs from CNT/SDBS/PEI film.

Table 4.2. CNT films thickness for both p-type and n-type semiconductors. N-type films are thicker than the p-type samples due to the inclusion of PEI polymer which has a larger molecular chain.

<table>
<thead>
<tr>
<th>CNT films</th>
<th>Film thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDBS p-type</td>
<td>22.9 ± 2.3</td>
</tr>
<tr>
<td>SDBS n-type</td>
<td>58.8 ± 3.8</td>
</tr>
<tr>
<td>SDS p-type</td>
<td>42.2 ± 3.2</td>
</tr>
<tr>
<td>SDS n-type</td>
<td>40 ± 3.1</td>
</tr>
<tr>
<td>X-405 p-type</td>
<td>45.9 ± 3.4</td>
</tr>
<tr>
<td>X-405 n-type</td>
<td>50.1 ± 3.5</td>
</tr>
<tr>
<td>Tween80 p-type</td>
<td>47.1 ± 3.4</td>
</tr>
<tr>
<td>Tween80 n-type</td>
<td>73.9 ± 4.3</td>
</tr>
<tr>
<td>F-127 p-type</td>
<td>24.8 ± 2.4</td>
</tr>
<tr>
<td>F-127 n-type</td>
<td>42 ± 3.2</td>
</tr>
<tr>
<td>B58 p-type</td>
<td>33 ± 2.8</td>
</tr>
<tr>
<td>B58 n-type</td>
<td>43.3 ± 3.2</td>
</tr>
<tr>
<td>ADBAC p-type</td>
<td>34 ± 2.9</td>
</tr>
<tr>
<td>ADBAC n-type</td>
<td>39.8 ± 3.1</td>
</tr>
</tbody>
</table>
4.3.2 Raman analysis

In addition to the SEM analysis of the CNT films and to further understand the effect of the surfactants on the CNTs, Raman spectroscopy was performed on both p-type semiconductors (CNT/Surfactant) and n-type semiconductors (CNT/Surfactant/PEI), for all surfactants as seen in Appendix D. The resulting signals were normalised to the G Peak intensity and compared to the signal of a raw CNT film.

The G band is related to the vibrations of the carbon atoms along the CNT plane structure. It is observed that the defect peak which is located between 1290 cm\(^{-1}\) and 1296 cm\(^{-1}\), shows small changes in the intensity. This confirms that the doping of the CNTs was achieved via non-covalent bonding to the structure, causing only small lattice imperfections to the CNT walls for the majority of the surfactants. The same is observed when adding 1 wt% PEI. Consequently, analysing the D peak has revealed small variations as a function of functionalization, where the values vary between 0.07 to 0.23. This is still a low range, indicating the good quality of the CNTs, and that no significant damage has been caused to the lattice of the CNTs which otherwise could negatively impact the electrical conductivity of the CNT films.

After analysing the pristine CNTs in Section 4.1.3, we determined that the crystal structure of the nanotubes is of high quality, with a low density of defects, as indicated by the small \(I_D/I_G\) ratio as seen in Figure 4-11. Firstly, a reference \(I_D/I_G\) range centred around 0.15 (\(I_D/I_G\) of raw CNTs) is considered in order to make a systematic comparison. We note that one of the major mechanisms for introducing lattice defects is ultra-sonication [163][164][165], which takes place during the addition of surfactants. For anionic surfactants, SDBS p-type has the lowest \(I_D/I_G\) ratio which signifies a low number of defects. It can be observed that for both SDBS and SDS, PEI inclusion has reduced the quality of the CNTs. As for non-ionic surfactants, Triton X-405 and B58 CNT films are clustered together for both p and n type materials with minimal variations in the \(I_D/I_G\) ratio. This indicates that both of these surfactants didn’t cause any defects to the graphitic structure of the CNTs while at the same time, adding PEI, resulted in no change to the \(I_D/I_G\) ratio. On the other hand, the cationic surfactant ADBAC has significantly reduced the quality of the CNTs by introducing defects. This is because CNTs are naturally p-type, therefore, adding cationic surfactants strongly affects the outer CNT structure.
According to Matarredona et al [16], it is believed that depending on the pH of the surrounding environment, CNTs can exhibit either a positive or a negative charge. Also, CNTs interact with the hydrophobic end of the surfactant. Thus, if the CNT outer structure is polarised, the Coulombic repulsion or attraction forces between the CNT wall and the charged hydrophilic groups of the surfactant can occur which can significantly increase solubility. Adding PEI to the mixture has significantly increased the quality of the CNTs which acted as a binding chemical agent at the defect sites.

\[ \text{Figure 4-11. Graph displaying the } \frac{I_D}{I_G} \text{ ratio of the CNT films (open symbols are for p-type CNTs and closed symbols are for n-type CNTs); the low values obtained are a strong indication of good quality CNTs. SDBS p-type film shows the lowest ratio due to the low density of defects. ADBAC p-type film has the highest ratio, but when adding PEI, the } \frac{I_D}{I_G} \text{ ratio drops significantly meaning that PEI acted as a binding chemical agent.} \]
After analysing the quality of the CNTs by looking at the \( I_D/I_G \) ratio, we now look at the degree of dispersion of CNT bundles. This is achieved by assessing the effect of surfactants on the frequency shift of the Raman G peak; this is because the hydrophobic end of the surfactant bonds with the outer structure of the CNTs. As discussed in Chapter 2 (Section 2.5.4), CNTs in their natural state after synthesis are closely packed together in bundles due to Van der Waal forces [98]. A bundle of CNTs can have any number of entangled CNTs, agglomerating together with an attraction energy estimated to be 500 eV/μm of tube-tube contact [167][168]. In order to disperse CNTs in water, surfactant molecules are directed in a way that allows their hydrophobic tails to face toward the CNTs while the hydrophilic ends are facing towards water as shown in Figure 2-20 in Chapter 2 (Section 2.7.4).

As a result, the surfactant’s main role is to separate CNT bundles during the ultra-sonication process in order to obtain CNT films after vacuum filtration, therefore, the reason for this analysis is relating the dispersion to the G peak wavenumber. This will cause a red shift in the G peak frequency as shown in Figure 4-12.

It is known that the G peak is associated with the longitudinal optical (LO) phonon mode in which the vibrations occur along the nanotube axis [169]. Its wavenumber \( \omega_{G^+} \) is sensitive to the addition of dopants during the charge transfer between carbon atoms and, in this case; surfactants and PEI, where the blue shift is for acceptors (holes/p-type) and red shift is for donors (electrons/n-type) [170].

Generally, it is thought that because the hexagonal units of hydrophobic chains match well with the carbon unit cells, the hydrophobic tail groups tend to lie flat on the CNTs surface [171]. Therefore, the hydrophobic tail length of a surfactant greatly affects the molecules absorption and consequently the dispersion.

The data from Figure 4-12 gives a comparative Raman analysis of the CNT films dispersed using the surfactants listed in Table 4-1 in Section 4.2, and the PEI doped CNTs. It is noticed that the G peak frequency shift ranges from 1587 cm\(^{-1}\) to 1583 cm\(^{-1}\) for all the CNT/Surfactant mixture. Furthermore, the degree of dispersion can have a direct impact on the homogeneity and stability of the CNT film, therefore, a valid method of analysing the state of dispersion is by visual inspection [172]. For example, the G peak frequency for the pristine CNT film is at 1587 cm\(^{-1}\); this has resulted in poor mechanical properties that can be observed on the CNT film as shown in Figure 4-1 in Section 4.1.1 where cracks are visible. As a result, it can be
stated that this difference in the Raman shift confirms that the CNTs in solution are dispersed whereas pristine CNTs are entangled, forming bundles due to Van der Waal forces. The G peak frequency of all the surfactants has red shifted as compared to the raw CNTs. For the p-type CNT component of the thermoelectric device, we can observe that SDS shows the largest shift at \( \sim 1583 \text{ cm}^{-1} \) where we can conclude that the level of dispersion for this surfactant is the highest. For the n-type functionalized CNT, the largest shift is obtained for Pluronic F-127. For

![Figure 4-12](image_url)

*Figure 4-12. Plot showing G peak position of raw CNTs and CNT films (open symbols are for p-type CNTs and closed symbols are for n-type CNTs), for Non-ionic and cationic surfactants a red-shift in frequency is observed when comparing p-types to n-types. Additionally, when looking peak frequency shift of the raw CNTs compared to the CNT/surfactant samples, we can see a red-shift which prove that the CNTs have been dispersed.*
non-ionic surfactants, a trend can be observed where each n-type component is showing a further red shift of the G peak when compared to their respective p-type materials. This indicates that the PEI can interfere with the optical phonon mode between the A and B unit cells of the carbon atoms [35] or the vibration frequency of the hexagonal lattice by attaching to it and making it heavier.

The latter analysis results from the fact that the G peak is associated with the longitudinal optical (LO) phonon mode in which the vibrations occur along the nanotube axis [169].

To summarise, we noticed that the surfactants show a blue shift as a result of the positive charge carriers (holes) and a red shift due to the negative carriers (electrons) when functionalizing using PEI except for anionic surfactants where PEI inclusion has resulted in a frequency blue shift. This could be explained by the way the surfactants molecules are attached to the CNTs structure which do not couple well to PEI molecular chains.

In all cases, and by visually analysing all the aqueous CNT/surfactant solutions, it can be confirmed that the CNTs did not agglomerate due to the uniform suspension of the CNTs in water.

After analysing the D peak and the dispersion of the CNTs as a function of the G peak frequency shift; we now look at the RBM peaks to characterise the CNT diameters and the structural properties of the DWCNTs.

Raman confirmed that the tubes are the same type of CNTs for all the surfactants as compared to the raw CNTs (Section 5.1.3); since all the peaks have appeared at the same wavenumbers in the RBM region, meaning that there is no change in the diameter, as seen in Figure 4-13. Referring back to the Kataura plot in Figure 3-18 in Chapter 3 (Section 3.4), it can also be confirmed, when using a laser energy of 1.58 eV for acquiring the Raman signals of the CNT films that the CNT diameters fall in the same area as the plot where we can see that the CNTs used for this chapter are a mixture of metallic and semiconductor tubes. The diameter range that applies to this case goes from 0.92 to 1.62 nm, which is typical of single and double walls (1.65 nm is either a CNT, or DWCNT, where 0.92 nm is the inner tube, within experimental error), however, wider tubes, or tubes that are not resonant with 1.58 eV are undetectable for this particular laser.
Figure 4.13. Raman spectra of seven surfactants (both p-type and n-type semiconductors) at the RBM region of the samples aligned against each other shows roughly the same peak positions as the raw CNTs which indicates that it is the same CNTs coming from the same batch; this is expected because the RBM corresponds to the vibrations in the radial direction of the carbon atoms, so any functionalization using surfactants happens on the outer shell of the tubes, thus, it should have no impact on the diameter of the CNTs.

Previously, a description was given on the G peak shift which confirmed the efficiency of a surfactant in dispersing CNTs by showing a red shift when compared to the raw CNTs wavenumber at 1587 cm$^{-1}$. In addition to that, the $I_D/I_G$ ratio of ADBAC p-type was estimated to be the highest at 0.23 which indicates a higher density of defects. On the other hand, SDBS p-type was measured to be the lowest $I_D/I_G$ ratio at 0.1. Therefore, to comprehend potential reasons for such a difference in CNT quality, a further analysis is required by looking at the RBM region and more specifically the intensity of each of the Raman signals originating from the inner and outer walls of the DWCNTs. It is known that peak intensity changes in the RBM are a consequence of the optical transitions at the density of states [173]. So it was observed
from Figure 4-13 that the two most dominant peaks in terms of intensity are the outer wall (1.62 nm in diameter) and the inner wall (0.92 nm id diameter), this means that the majority of the CNTs detected by the Raman laser are DWCNTs. Therefore, comparing the ratio of the inner and outer wall of the DWCNT Raman intensities of each CNT film, we can observe which CNT shell is more dominant as well as looking at the possible effect of each surfactant as seen in Figure 4-14. For example, raw DWCNTs display a ratio of ~ 1 where the intensities of both inner and outer walls are equal; thus, we can use it as a reference point when comparing the rest of the samples. The most noticeable ratio of 2.5 is for SDBS p-type CNTs, which shows a higher contribution of the inner wall. This could be correlated with the fact that the quality of the CNTs found in this sample show a value of 0.1. Consequently, this could mean that the higher RBM Raman intensity of the inner wall indicates that the outer wall has been significantly affected whereas the inner wall has remained intact. Furthermore, it is believed that the strong absorption onto the graphitic surface of SDBS molecules is due to hydrophobic tail group containing the benzene ring which relies on π-π stacking interaction [158]; this could potentially mean that the outer DWCNT shell has been damaged. Another reason could be that the strong π-π bonding has dampened the radial vibrations, reducing the intensity of the RBM peak. In other words, the surfactant wraps around the outer shell resulting in a decrease to its vibration amplitude and possibly changing the vibrational energy. On the other hand, adding PEI, SDBS n-type shows a decrease in the DWCNT walls RBM ratio which means that the polymer has attached less tightly to the outer shell causing an increase in the outer wall presence by reducing the number of defects. Another sample to notice is ADBAC p-type CNTs which has the highest $I_D/I_G$ ratio, indicating a high number of defects. The inner/outer wall RBM ratio of 0.57 signifies that the inner wall is more affected than the outer wall. This could possibly be due to the molecule size of 175 pm where the negatively charged chlorine molecule can be sucked inside the DWCNT, therefore, an interaction happens with the inner wall causing defects to its graphite structure. Furthermore, there is a possibility that the high compression from the surfactant hydrophobic tail is due to the strong binding that dampens the inner tube.

For non-ionic surfactants, it is observed that there are small variations between the p-type and n-type at ratios below 1 (except for p-type X-405) which means a stronger interaction with the outer walls.
In conclusion, we can assume that a higher inner/outer tube RBM peak ratio would indicate that the strength of the surfactant-interaction is stronger or weaker. This is also confirmed by the quality of the CNTs which suggests that a lower $I_D/I_G$ ratios is in agreement with a higher Inner/Outer wall RBM intensity ratio.

![Graph showing the ratio of DWCNT shells of the inner to outer wall for various surfactants.](image)

*Figure 4-14. Ratio DWCNT shells of the inner to outer wall (open symbols are for p-type CNTs and closed symbols are for n-type CNTs). A higher ratio means a higher intensity of the inner wall compared to the outer wall, meaning that the inner walls are undamaged and vice versa.*
4.3.3 TGA analysis of surfactants and PEI

In addition to the electrical property analysis above, TGA was conducted on each surfactant as well as PEI in order to assess their thermal degradation point and any residual particles remaining. Moreover, this thermal analysis will help in identifying which surfactant would be ideal especially when considering high temperature applications. Therefore, it is essential to estimate the residual content left at the oxidation/evaporation temperature points because a TE device generates a higher voltage when exposed to high temperature gradients. Figure 4-15 and Figure 4-16 display the TGA curves of the 6 surfactants used and PEI.

As seen in Table 4-1, the six surfactants that were used for TE device fabrication are classified into two categories: anionic and non-ionic, where the anionic ones (SDBS and SDS) contain sodium ions which show metallic behaviour. Therefore, it is expected that they would leave significantly more residue than the non-ionic surfactants, which can be seen from the TGA results shown below. Both SDBS and SDS have over 33% and 25% residue left in air respectively, compared to virtually no residues remaining for non-ionic surfactants. These residues left in anionic surfactants can be correlated with the high electrical conductivities obtained as seen in Figure 5-2; this means that these sodium-containing residues are reducing the distance between tube-tube contacts by potentially acting as metal connectors resulting in large conductivities but low Seebeck values.

On the other hand, non-ionic surfactants have very low residues left when TGA is done in air with Triton X-405 showing the lowest value at 0.12%. Here, a correlation can be made between the residues left and the Seebeck values; we can observe that the Seebeck voltage is indirectly proportional to the residual particles left (low residue mass results in a high Seebeck coefficient).
Figure 4-15. TGA data for non-ionic and anionic surfactants used to disperse the CNTs, analysed in both air and Nitrogen environments. Non-ionic surfactants produced the best results with Triton X-405 producing the least amount of residue in air at 0.12%. Anionic surfactants left the largest amount of residual masses due to their sodium contents [141].
As for PEI, which is the only polymer in this project used to functionalize CNTs into n-type semiconductors; TGA reveals that at 650 °C, there is a very low residual left with 0.27 % in air and 0.24 % in nitrogen.

In summary, it was shown that the non-ionic surfactants are ideal materials for CNT dispersion due to their low residual content in comparison to the anionic surfactants. However, it is noted that all the non-ionic surfactants as well as PEI have lower evaporation points compared to raw CNTs as seen in Figure 4-6 in Section 4.1.4 where the oxidisation temperature is ~ 590 °C. This can be advantageous if the CNTs are needed to be recovered within a standard oven that doesn’t require a vacuum environment, and thus reducing the process cost for commercial purposes such as CNT alignment processes [141]. However, in this situation, if the CNT films were to be used for temperatures higher than that of the respective evaporation point of the surfactants then this can cause the film to deteriorate (shrinking) and lose its mechanical integrity causing a short circuit therefore loss of output power.
5 Thermoelectric properties of CNT films

After the Raman analysis of the raw CNTs and doped CNTs (p-type and n-type), we determined the various effects that the surfactants and PEI have on the CNTs, mainly seen from the shifts in the G peak. Now, we will look at two important ZT parameters, the Seebeck coefficient (Figure 5-1) and the electrical conductivity (Figure 5-2) measured using the Van der Pauw technique (Raw data in Appendix B) and the Transmission Line Method. Thermogravimetric Analysis (TGA) (Figure 4-15 and Figure 4-16) was also performed on the surfactants in both Nitrogen (N₂) and Air in order to determine their thermal degradation stages and whether any residual masses were left. During the experimental phase of cutting the CNT films into small dimensions in order to make TE devices, the cationic surfactant ADBAC did not produce a rectangular film. This is because the integrity of the film didn’t hold causing it to break apart, therefore no Seebeck voltage and electrical conductivity values could be obtained.

5.1 Seebeck coefficient and electrical conductivity

From Figure 5-1, the most striking observation to make is the successful conversion of the p-type CNTs to n-type CNT films after inclusion of PEI. This is seen from the negative Seebeck values which prove that the majority charge carriers (electrons) have gathered to the cold end due to thermal diffusion, thus resulting in a negative potential difference. Next, we notice that the effect of PEI shows that most n-type materials have lower electrical conductivity values (ranging from 1.0E+03 to 3.6E+03 S/m, see Figure 5-2) than their respective like-for-like surfactant p-type semiconductors. This is likely caused by the electrically insulating properties of the polymer resulting in an increase in the distance between CNTs and in the narrowing of the electronic transport channels causing a reduction in their conductivity.

Figure 5-2 (b) shows that the TLM method is giving similar results for the conductivity as the van der Pauw method, and either can be used; however, once metal contacts are deposited on the film for the TLM method, that film cannot be directly used to manufacture a TE devices, therefore the van der Pauw method was preferred.
Firstly, we notice that the best Seebeck coefficient of a p-type material for anionic surfactants is CNT/SDBS with ~ 55 µV/K compared to ~ 39 µV/K for SDS; these values are not among the highest of all the surfactants in previous work [136]. However, their electrical conductivities are the highest with 2.6E+04 S/m and 1.7E+04 S/m respectively, which is due to the sodium ions contained. This shows that the CNT/Anionic films have an ionic conductivity (metallic characteristic, which means a high concentration of charge carriers. Another possible reason for a low Seebeck coefficient is the large residue present (TGA data in Figure 4-15: 33.1% for SDBS, and 25.1% for SDS in air) which could negatively impact the charge carriers when they drift, due to the induced temperature gradient. On the other hand, the highest non-ionic surfactant Seebeck voltage of ~ 82 µV/K is for the CNT/Triton X-405 film and an electrical conductivity of one order of magnitude lower (3.7E+03 S/m) than CNT/SDBS. This could be due to a lower carrier concentration and a larger effective mass of the charge carriers [9] in addition to virtually no residue present when the non-ionic surfactants oxidise as shown in Figure 4-15 (0.12% residue left for Triton X-405). Another interesting phenomenon occurred with CNT/Pluronic-F-127 film, where the Seebeck coefficient is significantly lower (~ 28 µV/K) than the n-type CNT/Pluronic-F-127 film, this can be explained from observing the doping experimental process in which Pluronic-F-127 is known to form a gel at temperatures above 10 °C according to its data sheet [174]; this is seen from the glossy smooth texture of the film after the vacuum filtration. However, this can have a positive effect when adding PEI to the CNT/Pluronic-F-127 aqueous solutions and stirring it at 55 °C, where the properties of a jelly-like material can adhere extremely well with PEI molecules and thus enriching the final film with additional charge carriers resulting in a higher Seebeck coefficient of ~ 70 µV/K.
Figure 5-1. Column graph of the Seebeck coefficient as a function of CNT films for two main categories of surfactants, anionic and non-ionic. SDBS and SDS CNT films show low values due to their high concentration of charge carriers. Triton X-405 CNT films show the highest values due to their low carrier concentration and large effective mass which is discussed in Section 5.2.
Figure 5-2. (a) Column graph of the electrical conductivity (Van der Pauw) as a function of CNT films for two main categories of surfactants, anionic and non-ionic. SDBS and SDS CNT films show the highest values due to their high concentration of charge carriers because of the sodium ions. All the non-ionic surfactant CNT films show significantly lower values due to their low carrier concentration, (b) shows the comparison between the Van der Pauw method (black bars) and TLM method (red bars) showing that the TLM line may also be used to estimate the electrical conductivity.

A further aspect of these measurements to analyse is the length of the hydrocarbon chain of both anionic and non-ionic surfactants; we notice from their chemical structure as seen in Figure 4-7 that SDBS and SDS contain a hydrophobic chain of 10 hydrocarbons (CH₂). On the other hand, Triton X-405 has the shortest hydrocarbon chain among non-ionic surfactants, whereas Tween 80 and Pluronic F-127 have the longest chains. In general, there are various effects of the nature of the hydrophobic group that should be taken into consideration when interaction between two materials happen (surfactant and CNTs). For example, by increasing the length of the hydrophobic group, this tends to decrease the solubility of the surfactant in water and increases its solubility in organic solvents [67]. In addition, it can cause closer packing of the surfactant molecules at the interface therefore forming micelles. Consequently, the melting point of the surfactant and of the absorbed film increases. However, introducing branching into the hydrocarbon chain of a surfactant such as Tween 80 and Pluronic F-127 can contribute in increasing its solubility in water. So in conclusion, the
The highest Seebeck coefficient obtained for CNT/Triton X-405 (81 µV/K) film may be related to its short hydrophobic end. Whereas CNT/Pluronic F-127 has the lowest Seebeck value due to its very long hydrophobic tail.

After the TGA analysis which contributed in assessing the dopants used in the TE device fabrication, one of the key parameters in the ZT equation in addition to the output power generated from each TE device can now be discussed. Figure 5-3 below describes the numerator of the ZT formula as seen in Equation 2-4 in Chapter 2 (Section 2.3). A first glance, the graph shows that the highest power factors are CNT/SDBS (~ 67 µW m⁻¹K⁻²) and CNT/SDS (~ 26 µW m⁻¹K⁻²) p-type films; this is expected due to their large electrical conductivity which is the dominating parameter in the power factor. This is among the highest reported values compared to previously published work (26, 38 and 33 µW m⁻¹K⁻²) [135][136][175]. On the other hand, non-ionic surfactant CNT films result in a significantly low power factor compared to the anionic films which is a consequence of the low number of the charge carrier concentration (low electrical conductivity) as it will be explained further down in equations 5-1 and 5-2.

![Figure 5-3. Plot of power factor as a function of CNT films. SDBS shows the highest power factor due to its high electrical conductivity. Triton X-405 is the highest among non-ionic surfactant due to its high Seebeck coefficient and electrical conductivity.](image-url)
This Section discusses the fabrication process of a TE device. Following the electrical characterisation of all CNT films semiconductors (p-type and n-type), a TE device for each surfactant can now be implemented in order to assess its output performance. The requirements of such a device is p-type and n-type CNT films connected electrically in series and thermally in parallel as illustrated in Figure 5-4 (a) – (b). This arrangement of elements allows the holes and electrons to diffuse under a thermal energy source (hot side) supplied by a platinum resistor $T_H$ whose temperature is controlled by a constant input voltage. On the cool side, the charge carriers will accumulate resulting in a net charge producing an electrostatic potential. However, even though the misaligned network of CNTs is demonstrated to stop the heat flux after 1 cm as seen in Figure 3-11 in Chapter 3 (Section 3.2), to prevent thermal equilibrium within 1 cm of the film, the temperature at the cold side needs to be maintained using a second platinum resistor $T_C$. The resistor is only thermally connected (to avoid a short circuit) to both sides of the copper tapes using a rectangular shape $\text{Al}_2\text{O}_3$ plate in order to consistently maintain a temperature gradient across both semiconductors as shown in the inset of Figure 5-4 (b).

Furthermore, the highly electrically conductive copper tape in the hot side is used to connect both semiconductors in order to form a p-n junction without direct recombination of both materials (forming a diode) as explained in Chapter 2 (Section 2.2).
In addition to the power factor calculations, the output power generated was measured using the Keysight B2900a by continuously running multiple IV sweeps (10 repetitions) across a voltage range; this way, the power and resistance can be calculated and plotted as shown in Figure 5-5.

From the above discussion in relation to the power factor, it can be concluded that just because the electrical conductivity is high or the Seebeck voltage is high, does not necessarily mean that the output power generated form a TE device made of both p-type and n-type semiconductors would result in a high output power; this is because a compromise must be found in thermoelectric materials between a large Seebeck coefficient and a high electrical conductivity. As it is highlighted in Figure 2-7 in Chapter 2 (Section 2.4), the peak value for ZT is obtained at a carrier concentration of $1 \times 10^{19}$ cm$^{-3}$. This means that highly conductive materials can negatively impact the ZT value therefore a balanced must be struck for optimum values. As seen from Figure 5-5 below, CNT/Triton X-405 TE device has the highest output power at 45 K temperature difference with approximately $\sim 67$ nW at an optimum load resistance of $\sim 65$ $\Omega$. This large value is in correlation with its high Seebeck coefficient demonstrating the importance of the low concentration of charge carriers. A further explanation to why SDSB and SDS CNT films show low output powers is that the high electrical...
conductivity caused by the high sodium content results in a high thermal conductivity which will adversely affect the voltage generated by preventing a large thermal gradient to occur. Since thermal conductivity is the contribution of both the charge carriers transporting heat ($\kappa_e$) and the phonons travelling through the lattice ($\kappa_l$), this means that any metal-like material (in this case, contains sodium) will have its high electrical conductivity directly related to $\kappa_e$ as seen from the Widemann-Franz law as shown in Equations 2-27 and 2-28 in Chapter 2 (Section 2.8.2).

Furthermore, it is known that a material with high carrier concentration has a high electrical conductivity and a low Seebeck coefficient and vice versa. This interrelationship between charge carrier concentration and Seebeck coefficient is highlighted in the equations below [9]:

$$\alpha = \frac{8\pi^2 k_B^2}{3 e h^2} m^* T \left( \frac{\pi}{3 n} \right)^{2/3}$$  \hspace{1cm} \text{Equation 5-1}

$$\sigma = n e \mu$$ \hspace{1cm} \text{Equation 5-2}

Where: $\alpha$ is Seebeck coefficient, $k_B$ is Boltzmann constant, $h$ is Planck’s constant and $m^*$ is effective mass of the charge carrier.

Equations 5-1 and 5-2 can be further analysed by discussing the parameter of effective mass $m^*$ which in simple terms relate to the weight of the charge carrier. It can be noticed that a high Seebeck coefficient is produced due to large effective masses but results in a low electrical conductivity. It is believed that heavy carriers will move slower thereby with smaller mobilities, which leads to a low electrical conductivity [9]. In conclusion, a compromise needs to be taken into consideration because a large Seebeck coefficient is obtained from a low carrier concentration material but at the same time, the large effective mass of the carrier will have low velocity that will induce low mobility.
Figure 5-5. A graph displaying the output power for the surfactant CNT films as a function of resistance at a temperature difference of 45 K. The highest value is represented by Triton X-405 due to its high Seebeck coefficient and low residual content.

From the output power data obtained, Triton X-405 has produced the highest value, therefore, it was compared against other TE devices that have been reported previously as seen in Table 5-1. From the results obtained in this project, we can observe that our findings are comparable and competitive in terms of the output power generated which is estimated to be 1.48 nW/K. To put this value into context, we look at different groups and what has been achieved. For example, Nonoguchi et al [135] compared 33 compounds which act as dopants in order to disperse CNTs and add charges to their structure which alters the electrical properties of the CNT films. It was found that tpp-doped SWCNTs and TCNQ-doped SWCNTs resulted to a ZT of 0.073 and 1.8 nW/K. This high value could be attributed to a different chemical structure of the dopants which can strongly bond to the outer structure of the CNTs, thus, increasing the charge density and the electrical conductivity.
Table 5-1. Comparison of triton X-405 performance against reported values by different groups.

<table>
<thead>
<tr>
<th>Author/Year</th>
<th>Description</th>
<th>Electrical conductivity (S/m)</th>
<th>Seebeck coefficient (µV/K)</th>
<th>Power factor (µW/mK²)</th>
<th>Output power (nW)</th>
<th>Temperature difference (K)</th>
<th>Power/Kelvin per p-n pair (nW/K)</th>
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<tbody>
<tr>
<td>Kim et al, 2010 [138]</td>
<td>p-type/PEDOT:PSS</td>
<td>40000</td>
<td>25</td>
<td>26</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hewitt et al, 2011 [137]</td>
<td>p-type/PVDF</td>
<td>298</td>
<td>15</td>
<td>0.06</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Hewitt et al, 2012 [137]</td>
<td>p-type/PVDF n-type</td>
<td>500</td>
<td>10</td>
<td>0.06</td>
<td>3.8</td>
<td>50</td>
<td>0.076</td>
</tr>
<tr>
<td>Nonoguchi et al, 2013 [135]</td>
<td>p-type/TCNQ n-type/tpp</td>
<td>9600</td>
<td>52</td>
<td>26</td>
<td>36.6</td>
<td>20</td>
<td>1.8</td>
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<tr>
<td>Lae Kim et al, 2014 [136]</td>
<td>p-type/SDBS N-type/PEI+DETA</td>
<td>11000</td>
<td>97</td>
<td>103</td>
<td>25</td>
<td>32</td>
<td>0.78</td>
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<td>Nakai et al, 2014 [175]</td>
<td>p-type/ Sodium deoxycholate</td>
<td>1000</td>
<td>165</td>
<td>33</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Avery et al, 2016 [176]</td>
<td>p-type/Fluorene based polymers</td>
<td>$10^1 - 10^5$</td>
<td>10 - &gt;1000</td>
<td>1 - 340</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Choi et al, 2017 [139]</td>
<td>p-type (CNT yarn) n-type (CNT yarn)</td>
<td>$7.5 \times 10^5$</td>
<td>57</td>
<td>2387</td>
<td>17.5</td>
<td>5</td>
<td>3.5</td>
</tr>
<tr>
<td>Our best TE device</td>
<td>X-405 p-type X-405 n-type (PEI)</td>
<td>3704</td>
<td>81</td>
<td>24</td>
<td>66.8</td>
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</tbody>
</table>
On the other hand, looking at a different structure to the TE device, alignment can be an alternative to a network of CNTs in obtaining a higher power factor. For instance, Choi et al [139] synthesised CNT yarns using a floating catalyst method which uses methane, thiophene and ferrocene as a carbon source, promoter and a catalyst precursor at 1200 °C, respectively. The as-prepared CNT yarns are directly fabricated on a roller and composed of hundreds of threads. This synthesis process produces a much superior electrical conductivity due to an increased carrier mobility. However, such a design has a major drawback which is a high thermal conductivity estimated to be 51 W/m·K; nevertheless this was a densified yarn and it is expected therefore that the emission of heat, which we have argued in Chapter 3 (Section 3.2), to occur over longer length scales, which means devices may end up larger for an automotive application. Indeed, their higher output power is obtained for a small temperature difference of 5 K; whilst an output power is not reported for higher temperature differences, this is expected to be less due to the much increased heat flow, which increases the overall temperature of the device, rendering it less efficient. Therefore, we can conclude that a random network of CNTs may be a better option for large scale applications, where higher temperature differences occur, since it results in an optimum power factor without compromising the overall ZT.

5.3 Selection of highest performing TE device (Triton X-405/CNT)

As a consequence of the large output power obtained at an impedance of ~ 65.4 Ω, CNT/Triton X-405 was selected as the material of choice for making a TE generator made of 6 pairs of P-N semiconductors electrically connected in series. Even though all the TE modules were installed on an insulating Medium Density Fibreboard (MDF) for better handling in the outside lab environment, this TE generator can still be designed in a manner to take full advantage of the CNT flexible properties. An exhaust pipe was then used to simulate a temperature difference and produce an output voltage as shown in Figure 5-6. The resulting voltage was displayed on a TENMA multimeter, showing ~ 42 mV at ~ 87 °C temperature difference. This shows that by adding 100 pairs of P-N semiconductors, an output voltage of ~ 0.7 V can be achieved without still compromising the weight factor like the robust inorganic
TE materials present. Alternatively, the weight of Triton X-405 p-type and n-type films are ~ 1.5 mg and ~ 1.5 mg respectively (Total ≈ 3 mg). This means that for each 1 kg of CNT TE devices made with Triton X-405, the output power would be 0.02 W.

Looking at the Seebeck coefficient values for the constituent n and p-doped CNT with Triton X-405 (Figure 5-1), under optimum conditions, a 6-pair element would result in a voltage of ~72 mV generated at 80K temperature gradient (in vacuum), which suggests that the MDF construct and the measurement in air reduced the ‘ideal’ conditions to about 60% of the ideal voltage. Nevertheless, a better choice of materials and encapsulation such as lamination may significantly improve this compared to the laboratory test values.
Figure 5-6. (a) A TE device made of 6 pairs of p-n semiconductors obtained from dispersing CNTs in Triton X-405 then placed on a semi-circular MDF for better handling, (b) TE device used for generating 41.9 mV at ~ 91 °C temperature difference on an exhaust pipe of a motorcycle.

5.4 Effect of doubling CNT mass on electrical conductivity

In order to optimise the CNT films electrical properties, an investigation was conducted on the effect of fabricating thicker CNT films. The thicker films synthesis specifications were double the mass used for the thin samples. In other words, 0.55 g of wet cake (37.4 mg of CNTs). This amount of CNTs was then mixed with 0.374 g of surfactant in a beaker filled with 100 ml of distilled water. The results are shown in Figure 5-7. The data shows that for a thicker sample the electrical conductivity has dramatically reduced by one order of magnitude from $2.6 \times 10^4$ S/m to $7.3 \times 10^3$ S/m which indicates that the high sodium content which is a highly reactive metal has induced further contact resistances between tubes within the CNT sample. The same observation can be made for SDS. However, for non-ionic surfactants, the decrease in conductivity is not as significant as anionic surfactants; for instance, Triton X-405 for the thick films drops down from $3.7 \times 10^3$ S/m to $2.7 \times 10^3$ S/m,
which shows that the increase in the CNT amount has caused a slight decrease to the electrical conductivity due to the surfactant not contributing much to the contact resistance within the film. Additionally, the Seebeck coefficient of these thick samples was measured and it is shown in Figure 3-12 in Chapter 3 (Section 3.2), where the values show a decrease in comparison to the thin films meaning that the charge carriers mobility has been hindered due to the internal resistance between individual tubes as a result of an increase in the number of CNTs. This data can reveal that a thinner sample with less density of CNTs is an ideal scenario which would not only improved ZT parameters but also, reducing the manufacturing cost by using a lower CNT amount.

![Figure 5-7](image)

**Figure 5-7.** A plot highlighting the electrical conductivity for p-type CNT films functionalized with the surfactants. It shows the effect of doubling the mass on the electrical conductivity.
5.5 Summary

In this chapter, we discussed the fabrication of TE devices made of CNTs provided by Thomas Swan. We first analysed the pristine (raw) CNTs using SEM spectroscopy, Raman and TGA. This was followed by comparing the effect of seven surfactants from three different categories (anionic, non-ionic and cationic) used to disperse the CNTs and functionalizing them by adding PEI. The obtained solution was then vacuum filtered in order to get flat CNT films. The latter materials were then analysed by Raman which helped in understanding the effects of surfactants on the outer structure of the CNTs and the efficiency of dispersion. Furthermore, thermoelectric properties such as the Seebeck coefficient and electrical conductivity were measured and it was determined that the sodium content in anionic surfactants contributes positively to get a high electrical conductivity, however, it negatively impacts the Seebeck coefficient. On the other hand, non-ionic surfactants showed some of the highest Seebeck values especially Triton X-405 which resulted in a value of 81 µV/K and an output power of ~ 67 nW at 45 K temperature difference. Due to these high values, Triton X-405 CNT films were chosen to be the ideal material for the exhaust system application. Finally, an investigation was conducted on the effect of doubling the CNT content which showed that the metallic behaviour of SDBS and SDS has contributed to the increase in the film resistance causing the electrical conductivity to decrease.
6 Conclusion and Future Work

After recognizing the high energy demands of our modern society due to a larger population compared to the last decade and due to shortage of fossil fuels as well, scientific institutions have increased their efforts in developing highly efficient advanced materials as an alternative to current energy sources. These functional materials must meet certain criteria, such as having a very low environmental impact, high strength, long durability and low weight. This is why they are becoming increasingly the ideal choice of materials for modern applications. Therefore, a device that is capable of harvesting waste heat and converting it into useful electricity is an even better system to investigate. Such material is a “thermoelectric device” which applies the principal of the Seebeck effect in order to generate voltage. However, current TE devices available commercially in the market such as those made of Bi$_2$Te$_3$ are bulky, toxic and expensive to manufacture. This is where CNTs become an alternative option since they offer many possibilities to alter their thermoelectric parameters; Seebeck coefficient, electrical and thermal conductivity independently. The low dimensionality that they offer makes them an attractive material due to the possibility of inducing quantum effects to affect the phonon transport at the density of states.

CNTs are allotropes of carbon which is in the form of a rolled up sheet of graphene. They can be s-SWCNTs, m-SWCNTs, DWCNTs or MWCNTs. Each type presents different electronic characteristics which can be used for various applications. For example, metallic CNTs would be the perfect candidates for use as electrical connectors, whereas semiconductors can be used for making TE devices. The use of s-SWCNTs is the best option because they offer the optimum concentration of charge carriers, which results into the highest power factor along with an ideal thermal conductivity.

In this thesis, CNT synthesis using the PTCVD technique was explored. This system offers the option of a low temperature growth process which is beneficial for large scale applications, as well as vertical alignment. The investigation conducted in Chapter 4 has resulted in a high quality ($I_D/I_G$ ratio) of 0.07 and a height of 152 µm.

In chapter 5, TE device fabrication was explored in detail, where the CNTs used were high quality CNTs provided by Thomas Swan. The Raman characterisation confirmed the high quality of these CNTs which is 0.15 for raw CNTs.
In addition, the fabrication process of TE devices was performed with the use of 7 surfactants of different hydrophilic group polarity (anionic, non-ionic and cationic). The results obtained for the ZT parameters showed that anionic surfactants have high electrical conductivities due to their sodium content, but low Seebeck coefficients due to their metallic behaviour, which leads to a low thermal gradient. On the other hand, non-ionic surfactants exhibited the best Seebeck coefficient values due to their low concentration of charge carriers. This led to the selection of Triton X-405 as the ideal surfactant for dispersing the CNTs, thus, obtaining a thin film with a high power factor and a high output power of 66.9 nW at 45 K temperature difference.

Finally, all the characterisations carried out on the CNT films have contributed in achieving the main objective set for this project, which was fabricating a working TE device which can be used on a motorcycle exhaust and other applications to harvest waste heat.

For future work, it was determined that throughout the characterisations conducted on the CNTs, there were many examples of further investigations that can be carried out in order to optimise the ZT parameters. For instance, the CNTs used in Chapter 5 for the TE device fabrication were characterised by Raman to be mostly DWCNTs with a mixture of metallic and semiconducting CNTs. Since it is known theoretically that semiconductors are the ideal type of materials, it is worth exploring the possibility of reducing the number of metallic CNTs by the use of an electrical breakdown technique (burning off). This is because the presence of both type of conductors within a film would result in internal short circuits, therefore reducing the potential voltage generated. Another area to research is the CNT alignment in a film. This would greatly increase the electrical conductivity due to low contact resistance at the junctions between the tubes. However, this could significantly increase the thermal conductivity due to the direct phonon conduction at the DOS.
Appendices

I Appendix A: VACNTs synthesis and characterisation

I.I Introduction

CNTs can be grown in a number of ways as shown in the literature review in Chapter 2 (Section 2.5.2). These techniques include the arc-Discharge, laser-Ablation and chemical vapour deposition (CVD). Each of these techniques produce different types of CNTs. The quality of the CNTs synthesised by these methods can vary depending on the growth temperature. However, high temperature synthesis systems such as the arc-Discharge and Laser-Ablation would result in non-vertically aligned CNTs with high impurities, in addition to a large manufacturing cost. Consequently, it is important to optimise the growth process for a potential future thermoelectric application based on VACNTs.

Carbon nanotubes have a significant aspect ratio, making it possible to produce large numbers of CNTs within a small volume [177]. Therefore, it is necessary to use a system capable of synthesising vertically aligned CNTs in an organised manner. The PTCVD technique used in this project (described below in Section 1.2) allowed us to grow our own high quality CNTs with an I_D/I_G ratio as low as 0.071 with heights reaching 152 µm.

One of the characteristics in growing CNTs using a photo thermal system is obtaining VACNTs. This can be particularly useful if CNTs are to be used as thermoelectric elements which are arranged vertically, thus, resulting in high electrical conductivity due to the low contact resistance and the direct channelling of the charge carriers (no tube-tube contact). Although, the main purpose here is to explore the various properties of the CNTs (optical, quality, height, etc) that can be tuned and optimised depending on the application.

This chapter will outline the experimental methods used in the growth process of the VACNTs and their Raman characterisation. The three sub-Sections of this chapter are: the substrate and catalyst preparation, the CNT growth, the analysis technique (both optical and Raman).

In the first Section, the different layers deposited on a silicon substrate will be explained. The second Section describes the use of the PTCVD system and the various parameters implemented in the CNT synthesis. The last Section will show the characterisation of the as-grown CNTs that includes Raman spectra of each sample.

This analysis will lead us to understand the properties of the CNTs, and the importance of high quality CNTs which can be used for making thermoelectric devices as CNT films.
I.II Description of PTCVD system

In this project, the synthesis of CNTs was performed by photo-thermal chemical vapour deposition (PTCVD). As reported by Chen et al [49][178], this technique involves the use of high energy arrays of lamps directed downward on the substrate.

Figure I.1. Schematic diagram of the Photo-thermal CVD system 1000N includes; 8 IR lamps covered by a quartz glass, a substrate holder located above the water cooling line, an inlet for the reactant gases, and a pump [179].

As noted in Section 2.7.2, different methods for growing CNTs were introduced and discussed. Conventionally, there are two commonly used methods to grow CNTs which are the catalytic chemical vapour deposition (CCVD) and the plasma enhanced physical vapour deposition (PECVD). However, CCVD is a lengthy CNT synthesis technique due to the long process in reaching the optimum temperature and the time it takes for the chamber to cool down. On the other hand, PECVD reduces the quality of the CNTs due to the ion bombardment [180]. This happens during the sputtering process by which the substrate holder and the chamber wall exposed are affected resulting in impurities being deposited into the CNTs. Here, a different CVD design was adopted for the CNT growth known as photo-thermal CVD (PTCVD) [49]. The motivation behind this system is its compatibility with CMOS technology and its ability to grow CNTs over large-areas in excess of 4 inches at industrial scale. Moreover, the
capability of synthesising CNTs at low temperatures while maintaining the silicon substrate below 350 °C which was successfully achieved at the ATI by Chen et al [178]. This technology is based on a top down heating method where the energy is delivered using IR radiations from the top which will thermally activate the catalyst with the contribution of a carbon source [179].

This system is equipped with eight infrared (IR) lamps to control the temperature during the growth process. Figure I-1 shows a schematic of the PTCVD and the various modules which include: IR lamps installed on the top of the chamber covered and isolated by a quartz window, a pyrometer which monitors the temperature at the bottom of the substrate (named $T_s$), inlets and outlets for letting the gases in and for extraction and a water-cooled bottom plate [179].

In addition, this growth technique can not only deliver heat directly onto a cooled substrate, it can also produce vertically aligned CNTs which can be used as interconnects in CMOS technology and other electronic applications where alignment is required. This is achieved by controlling the formation of the seeds (iron catalyst) during the annealing process. For example, it has been reported that by Ahmad et al [181] that tuning the thickness of the Titanium Nitride (TiN) which is defined in the next Section, can result in a desirable catalyst diameter with a narrow distribution of the CNT. The higher density of the catalyst islands results in self-organisation of the CNTs into vertically-aligned forests, helped by the temperature gradient across the CNT (always hotter at the top of the film). This route of varying the TiN layer thickness has been employed in this work, however, a novel set of gas ratios is used which resulted in very low CNT quality which hasn’t been reported before.

I.III Preparation of substrate and catalyst

A silicon wafer was used as a substrate for the CNT growth, which is a very common material for this type of growth. In addition, TiN was employed in order to prevent the catalyst from diffusing into the silicon and consequently resulting in the formation of noncatalytic silicide, thus, it serves the purpose of a diffusion barrier [182][183]. As reported by Simmons et al, due to the increased kinetics, silicide has been shown to inhibit primarily SWCNT growth which is synthesised at higher temperatures rather than MWCNT [184]. Furthermore, according to Cao et al, it has been proved that increasing the silicon dioxide layer thickness
from 6 to 24 nm can result in a more efficient growth [185]. However, a silicon dioxide layer of that thickness can become an insulating layer which is not ideal for electronic applications. Therefore, to overcome this problem and to stop silicide formation, a layer of TiN is sandwiched between the silicon wafer and the catalyst, to improve CNT growth. In addition to its high electrical conductivity, TiN has also a good thermal stability [186][187].

Furthermore, the inclusion of aluminium oxide (Alumin(a) Al₂O₃ can stabilise and prevent the catalyst from coalescing into an island [187]. Consequently, after the deposition of the catalyst, such as Iron (Fe), a strong interaction between the catalyst layer and the oxygen atoms on the surface of alumina will lead to oxidation, therefore, a reduction process of the catalyst is required to enhance the growth efficiency [187].

In this project, Iron is used as the catalyst, deposited onto layers of aluminium, native alumina (Anchor layer) and titanium nitride (Thermal barrier layer) on a silicon wafer, as shown in Figure I-2 [188]. The thermal barrier which consists of the TiN layer; its role is to slow energy heat transfer to the Silicon substrate allowing it to be removed by the gases flowing in the chamber at high rate [49]. Additionally, when using the PTCVD system which involves Infrared Radiation (IR) supplied by 8 lamps, a reflector on the front surface is needed to reflect any radiation energy back to the catalyst to enhance the heating efficiency for an improved CNT growth, thus the need for TiN where 45% of IR light is reflected and less than 10% is transmitted [189].

<table>
<thead>
<tr>
<th>Iron (Catalyst)</th>
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<tbody>
<tr>
<td>Alumina (Anchor layer)</td>
</tr>
<tr>
<td>Aluminium</td>
</tr>
<tr>
<td>TiN (Thermal Barrier Layer)</td>
</tr>
<tr>
<td>N-type Silicon</td>
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*Figure I-2*. Structure of the substrate layers, TiN is deposited on n-type silicon wafer which acts as a thermal barrier, followed by an aluminium layer and its native oxide which is sputtered and acts as an anchor layer. Lastly, the Fe catalyst is deposited on top of the native alumina.
The TiN film was coated to a silicon wafer using a DC-sputtering system; this particular system includes a pump, a DC power supply and two electrodes (Anode and cathode). The process pressure which is several milli-torr can be controlled manually using the software provided. Consequently, a voltage across the electrodes strikes a plasma which strikes a target to generate clusters of the target material. In addition, argon (Ar) gas is used during the entire process in order to get a plasma.

The parameters used for the coated layers (TiN, Al, Al₂O₃) are: for TiN, sputtering power density of 3.2 W/cm², 25 sccm Ar, and 20 sccm N₂, in a vacuum pressure of 3.2×10⁻³ Torr, for 15 min (50 nm thickness) for a set of samples and 30 min (100 nm thickness) for another set. After TiN deposition, a 25 nm aluminium layer was deposited at a power density of 1.5 W/cm² under a pressure of 3.8×10⁻³ Torr for 2 min. As a result, once the substrate is taken out of the vacuum environment and exposed to oxygen, a thin layer of 5 nm native alumina is formed due to oxidisation in air. The latter layers (Aluminium and alumin(a) act as anchor layers as well as presenting an additional advantage in reflecting IR light back to the catalyst with over 90% reflectance for aluminium, which is beneficial even if alumina transmits over 90% in the IR range as shown in Figure I-3 [190]. The parameters used for the catalyst layer (Fe) are: sputtering power density of 0.37 W/cm², 25 sccm Ar, under 3.8×10⁻³ Torr of pressure for 1 min.

Regarding the catalyst deposition, it was reported by Hofmann et al that the growth rate of CNTs and the tube diameter are significantly affected by the catalyst film thickness, for example, a 1 to 2 nm iron layer thickness shows a growth rate of 12 nm/s and ~ 3 nm in diameter, whereas a 4 to 5 nm thickness decreases the CNT growth rate to 1 nm/s and a diameter of up to 100 nm [191]. Therefore, it can be assumed that SWCNTs are more likely to be obtained when using a thinner catalyst layer/islands.
Figure 1-3. Graph shows: (a) Reflectance of 25 nm aluminium where over 90% of IR light is reflected to enhance CNT growth [190], (b) Transmittance of 5 nm aluminium oxide where over 90% of IR is transmitted which in turn reaches the reflective layer (aluminium) [192].

I.IV VACNT fabrication using PTCVD

The chosen gases for the growth process are Hydrogen (H\textsubscript{2}) and acetylene (C\textsubscript{2}H\textsubscript{2}) which correspond to the carrier and reactant gases respectively. Prior to their introduction into the chamber, they are pre-mixed in the manifold where initially the acetylene is cleaned via a filter to eliminate acetone and reduce catalyst poisoning [131].

The first step is the reduction of the catalyst which lasts 5 min and requires the oxidised layer formed due to oxygen exposure to be reduced into metallic islands. The chamber is first pumped down to 5 x 10\textsuperscript{-5} Torr; once 94 sccm of hydrogen is introduced, the auto pressure baffle valve is set to maintain a constant pressure of 2 Torr. This is followed by turning on the IR lamps which are controlled by a digital temperature controller in order to reach 300 °C.

The second step is the CNT growth process which lasts in 10 min resulting in VACNT heights ranging from ~ 10 nm to ~ 119 nm. This stage involves introducing 6 sccm of the carbon feedstock in the form of acetylene. The same process pressure of 2 Torr is kept. The set power of the IR lamps was varied from 47.5% to 62.5% with 2.5% step, which is equivalent to T\textsubscript{s} varying between 380 °C to 490 °C at various temperatures/powers which will then be compared against their Raman results.

The third step is the cooling process in which the IR lamps are turned off and only hydrogen remains flowing inside the chamber at 2 Torr until a safe temperature is reached. In addition,
the system automatically introduces Nitrogen which will contribute to the cooling of the sample. Consequently, the sample can be taken out of the chamber.

I.V  VACNT characterisation

I.V.1 Optical characterisation

For this project, the TE modules are carbon based materials, so a potential future application could involve the use of a device structure such that its top surface is capable of absorbing light at a high rate is possible. Thus, for a carbon nanotube which is a black material, it has the ability to absorb ~ 99.9% incident light that falls on its surface across the whole electromagnetic spectrum for CNT thicknesses ranging between 10 – 800 µm [193]. The need for a highly absorbing surface is important because the photons collected from the wide spectral range causes the absorbing layer to heat up and this heat energy will in turn create a temperature gradient between the top surface and the bottom surface (heat sink) necessary for the Seebeck effect to happen. Therefore, the aim of characterising the optical properties of CNT’s is to determine the reasons for its high absorption (~ 99.9%).

Carbon nanotube forest is a near perfect black body material [194]. An ideal black body is the perfect absorber because all light that strikes its surface is absorbed and no light is transmitted or reflected, with an emissivity equal to 1.

Figure I-4 shows a forest of VACNTs grown on a silicon wafer. The need for vertically aligned nanotubes is their high interaction with incident light parallel to the tubes. Just by observing with the naked eye, it appears that all the VACNTs samples are black regardless of the change in the input power (temperature).

![Image of CNTs grown on silicon wafer at different power levels]

*Figure I-4. Optical Images of CNTs grown on silicon wafer at powers of: (a) SAM1 = 47.5%, (b) SAM2 = 50%, (c) SAM3 = 52.5% and (d) SAM4 = 55% display very high absorbing properties due to their very dark (black) surface.*
A VACNT forest has a remarkably high absorptivity in thermal equilibrium (373 K) compared to a standard black surface like a black paint. It varies from 0.98-0.99 in the electromagnetic spectrum range of 300 - 1800 nm as illustrated in Figure I-5. It shows that the four synthesised VACNT samples demonstrate that the absorption is almost independent of the wavelength across the whole spectral range. Due to the spectrometer limited sensitivity of its detector, the optical data of the VACNT samples for the Ultra-violet range (below 300 nm) cannot be obtained.

For an ideal black body, the absorptivity has to be unity across a very large spectrum range. However, for these measured samples, the absorptivity is around 0.98 for a limited spectral range which strongly suggests that the VACNT forest is a near black body. This absorptivity values were calculated using Kirchhoff’s law which states that the emissivity at temperature $T$ of a material equals its absorptivity at the same temperature [195]. The emissivity is unity subtracted from reflectivity, that is true if and only if, the transmissivity is zero; this is deduced from the sum of the three optical parameters (Absorptance + Reflectance = 1) [196].

Figure I-5. Graph shows the absorptivity of VACNT forest (red, blue, pink and black line) and a standard black paint on a plastic surface (green line) of 0.5 cm in thickness. The noise at around 800 nm is a caused as a result of a change in the detector/filter speed reading when measuring in the near-infrared range. The absorption is estimated from the reflection geometry only ($A = 1 - R$)
The reflectance properties were measured and the results from Figure I-6 show a very low reflectance with a range between 0 - 0.008. However, it is slightly flat across the spectrum range, in other words, the small variations in the measurements are probably due to artefact when changing the grating. It should be noted that the variations in these measurements occur at the edge of the visible/infrared regions (at 800 nm precisely). There are some irregularities which may have been caused by experimental uncertainties mostly during the calibration process when using the PTFE as a reference in addition to the change in the detection mode when performing measurements in the “Near-infrared” region where the average time for collecting data from the Carry 5000 detector is reduced to 1.0 seconds per short series of wavelengths.

![Reflectance characterisation of VACNT forests (SAM1, 2, 3 and 4) using the integrating sphere. The spectra is dominated at the 800 nm mark for a short range by artefact.](image)

*Figure I-6. Reflectance characterisation of VACNT forests (SAM1, 2, 3 and 4) using the integrating sphere. The spectra is dominated at the 800 nm mark for a short range by artefact.*

One factor leading to a high absorption rate in a VACNT forest is the transitions between the sharp peaks which are most notably known by “Van Hove singularities” (VHS) [173]. As discussed in Chapter 2 (Section 2.7.1), carbon nanotubes are a one-dimensional type of material, therefore, these transitions that occur at the density of states (DOS) between energy states (E11, E22, etc) result in different properties unlike conventional 3-dimensional
materials such as “bulk materials” where the DOS is a continuous function of energy [173]. The sharpness of these optical transitions lead to an easy photon-electron interaction within CNT atoms [173].

Another factor resulting in ≈ 99% absorption is the sparseness or low density within the VACNT forest. According to Futaba et al [197], the average SWNT diameter is 3.0(±0.07) nm, and an area density of 5.2 × 10^{11}(±0.35 × 10^{11}) tubes/cm^{2}. This means that within a substrate surface area of 190 nm^{2} and an average distance of 14 nm between tubes, the total volume occupied by the SWCNTs represents only 3.6%, therefore, ~ 97% is empty space. This particular property can suppress reflection which can be proved by applying Fresnel’s law [198]:

\[
R = \frac{(n-n_0)^2}{(n+n_0)^2}
\]

Where: R is the reflectance, n is the refractive index of a surface and \( n_0 = 1.0003 \)

In the case of a CNT forest, air has a refractive index of 1.0003 whereas most solids like CNTs are known to have a refractive index greater than 1.4, therefore, by just applying the above equation, the reflectance would be greater than 0.028 which would lead to a higher absorption [196]. In addition, the CNT forest appears homogenous as seen in Figure I-7 which is due to the thin distribution of the CNTs. The top of the VACNTs is shown to be a smooth flat and uniform surface with microscale imperfections (holes) which are caused by the absence of a catalyst, thereby, the carbon atoms from the acetylene cannot have any interaction. Moreover, the small distance separating the CNT bundles which can be referred to as interstitial regions is smaller than the wavelength (estimated to be 5-30 nm), thus, rendering optical transmission very low.
Figure I-7. SEM for VACNTs showing a very dense CNT forest closely packed together (bundles) which results in an extremely low reflectance, thus, a higher absorption.

The results presented above are almost similar to those presented by Mizuno et al [196]. The data presented by the group show that SWCNT have an emissivity of 0.98 - 0.99 across the UV-far IR. These properties will benefit TE generators made of VACNTs since a high absorption will maximise the temperature gradient across a TE device. Our values are close to Surrey NanoSystems where they have synthesised an extremely dark material (CNTs) called “Vantablack” which absorbs incident radiation at 99.965% [199].

In conclusion, the above results have proven that vertically aligned carbon nanotubes have some useful properties for potential future TE devices used as light absorbers, with an absorptivity close to unity. From an optical point of view, CNTs are black, owing their very low reflectance and high emissivity to the homogenous sparseness of the VACNT forest in addition to the uniform alignment structure which is critical in achieving a near black body.
I.V.2 Raman characterisation

From Chapter 3.4, a detail description of the Raman technique was provided where the different peaks associated with a typical Raman CNT signal are shown. For this Section, the quality of the nanotube will be determined as well as the type of CNTs, which can be either MWCNT or SWCNT (SWCNT can be either semiconducting or metallic), using “Raman spectroscopy”. This is particularly important if VACNTs are to be used as thermoelectric elements, because it a TE device requires both n-type and p-type semiconductors connected in series, thus, identifying the quality and the type of the CNTs is necessary.

The experimental work for this Section involves two groups of different thicknesses of titanium nitride layer, A1 is the set of samples which has 50 nm TiN layer whereas A2 has 100 nm TiN layer. The remaining growth parameters are the same as mentioned in Section 4.3

For this characterisation, the laser used was $E_{\text{Laser}} = 2.42 \text{ eV}$ which corresponds to $\lambda = 540 \text{ nm}$. This laser is able to detect both semiconducting (150-210 cm$^{-1}$) and metallic (210-280 cm$^{-1}$) SWCNT in the radial breathing mode (RBM) regions (150-300 cm$^{-1}$), unlike the red laser with $E_{\text{Laser}} = 1.58 \text{ eV}$ and $\lambda = 782 \text{ nm}$ which can only measure semiconducting SWCNT in the same region as seen in the Kataura plot in Chapter 3.4 [35] [49][200].

Our CNTs are synthesised using the PTCVD system as described by Shang et al [179]. Before proceeding to the SEM and Raman data analysis; first, a brief description is given on the growth model. Baker et al [201], suggested the “Volume diffusion model” which is based on a top-down heating operating method where the top surface of the iron catalyst is sufficiently heated to allow the carbon atoms dissociated from the acetylene molecules to interact with the catalyst islands. Since there is an induced temperature gradient within the catalyst; this leads the carbon atoms to migrate with high diffusivity to the bottom of the catalyst (colder side). As a result, the dissociated carbon atoms dissolve and diffuse into the catalyst (Surface diffusion or bulk diffusion) until a saturated state is reached [202]. A model is shown in Figure I-8 which was suggested by John Robertson [203].
Figure I-8. CNT growth model by Robertson displaying the tow different growth models, the carbon and hydrogen atoms are coloured in blue and white respectively and the black lines represent the CNT walls. (a) A tip growth where the carbon molecules diffuse around the catalyst resulting in the CNT lifting off the catalyst particle, as oppose to the root growth, (b) shows a diffusion process through the catalyst [203].

The CNT synthesis performed using the photo-thermal system has resulted in various CNT lengths. Using electron microscopy, CNTs grown on a Si substrate at temperature range between 380 to 490 °C are shown in Figure I-9. It can be observed from all the SEM images that perfect vertical alignment is achieved in all conditions regardless of temperature. However, it wasn’t possible to report any effect of the TiN thickness on the alignment of the CNTs for all the samples. A possible explanation could be that there is sufficient heat energy that allows the CNTs to grow in perfect alignment.
(a) TiN = 100 nm at 380 °C

(b) TiN = 50 nm at 380 °C

(a) TiN = 100 nm at 400 °C

(b) TiN = 50 nm at 400 °C

(a) TiN = 100 nm at 420 °C

(b) TiN = 50 nm at 420 °C
(a) TiN = 100 nm at 440 °C

(b) TiN = 50 nm at 440 °C

(a) TiN = 100 nm at 455 °C

(b) TiN = 50 nm at 455 °C

(a) TiN = 100 nm at 475 °C

(b) TiN = 50 nm at 750 °C
As mentioned in Section 4.2, the TiN layer main roles are: to act as a diffusion barrier layer and a thermal layer resulting in the prevention of silicide formation, thus, delaying the loss of heat energy, as well as reflecting long wavelength infrared radiation. Therefore, an assumption can be made that the CNT quality is directly related to the TiN thickness. A calculation of the $I_D/I_G$ ratio will shed light on the effect of the thermal barrier layer on the quality of the CNTs. This theory can be proved experimentally by varying the TiN thickness layer. The expectation from this work is a lower $I_D/I_G$ ratio for 100 nm layer and a higher growth rate compared to 50 nm layer.

A typical Raman signal from the as-grown CNTs by PTCVD would have several peaks similar to previously reported by Chen et al. This signal will provide details of CNTs as shown in Figure I-10. It can be noticed that there are well defined peaks in the first and second order Raman, where there is the D peak centred at 1340 cm$^{-1}$, and the G peak at 1580 cm$^{-1}$ and a 2D peak around 2680 cm$^{-1}$. These various peaks have been described in Section 3.4.
Each Raman signal from the VACNT samples (A1 and A2) is analysed from the cumulative peak which can be obtained using a model based on a Lorentzian function. Figure I-11 shows the $I_D/I_G$ ratio as a function of CNT growth temperature which indicates the quality (purity and defect density) of the as-grown VACNTs. Additionally, the type of CNTs can be inferred from analysing the RBM. For a consistent comparison between the samples, the Raman signals have been normalized to the G peak intensity [35]. The graph below describes the effect of the temperature on the $I_D/I_G$ ratio. An increase from 380 to 400 °C, where the $I_D/I_G$ increases to 0.21 and 0.29 for A2 and A1 respectively, then a sudden decrease to around 0.10, with the lowest $I_D/I_G$ ratio of 0.07 for A2. The latter value is the lowest recorded value when compared to other CVD techniques [204]. However, the best CNT quality synthesised using the PTCVD system reported by Ahmad et al [181] shows a value of 0.13 which is still higher than our best value of 0.07. Therefore the quality of the nanotubes is enhanced when the growth temperature is above a threshold value of 420 °C. Similarly, VACNTs grown at 475 °C show the lowest $I_D/I_G$ ratio for A2, indicating that it contains the
lowest number of defects compared to the other samples tested. However, the main observation from the graph is the consistent pattern of the CNT qualities when comparing A1 to A2; in all samples, the thick TiN (100 nm) layer has low/equal $I_D/I_G$ ratio as the 50 nm TiN layer. Overall, the low $I_D/I_G$ and the presence of a high 2D peak for all the Raman signals as shown in Appendix 3 is indicative of the high CNT quality which is due to the reflective properties of the TiN layer which can act as an additional control parameter on top of the gas (acetylene and hydrogen) ratios and the pressure.

![Graph showing $I_D/I_G$ ratio as a function of growth temperature for VACNT growth. The data shows that the thick reflective surface of TiN improves the quality of the CNTs.](image)

Figure I-11. $I_D/I_G$ ratio as a function of set power for VACNT growth. The data shows that the thick reflective surface of TiN improves the quality of the CNTs.

In Figure I-12, it was observed that the CNT growth rate as a function of temperature for both TiN layers. Over the whole temperature range, the growth rate varies from ~ 1 to ~ 12 µm/min for 50 nm TiN layer, and from ~ 2 to ~ 15 µm/min for 100 nm TiN layer. The key observation from the growth rate graph is first, an increase up until 420 °C for 50 nm and up to 440 °C for 100 nm followed by a decrease as a function of temperature increase. This is believed to be
caused by catalyst poisoning at higher temperatures [205]. This behaviour is similar to what has been reported in the literature [181].

Figure I-12. Growth rate of VACNTs as a function of temperature. The highest rate is attributed to the 100 nm TiN layer at 440 °C.

I.VI Summary

In this chapter, the PTCVD synthesis technique used for VACNT growth has been explored. A detail description on the layers deposited on the silicon substrate was provided which are the TiN, Al and Fe layers. In addition, the characterisation techniques used to analyse the CNTs were optical spectroscopy and Raman. It was concluded that VACNTs are extremely absorbing materials with more than 99.9% across the whole spectrum. Furthermore, the growth parameters chosen contributed in obtaining the best CNT quality with an I_D/I_G ratio of 0.07. This was also possible due to the 100 nm TiN thermal barrier layer which helped in reaching a very low defect density.
Finally, even though the PTCVD method presents many advantages in obtaining high quality CNTs and vertically aligned, there were some challenges that led to not using the as-grown CNTs, but instead, working on commercial CNTs (Thomas Swan) for the fabrication of the TE devices. Some of the difficulties include the reliability of the system in producing repeatable results. On numerous occasions, the system was not able to grow CNTs when using the exact same parameters and same catalyst conditions. This could well be attributed to many variables that will make it difficult to identify and fix the problem. Such variables include the acetylene cylinder which is located outside the building making the reactant gas temperature variant depending on the season. Also, the build-up of a carbon ash layer on the quartz glass which separates the IR lamps, thus, altering the intensity of the IR radiation and the ultimate substrate temperature. This carbon layer could not be cleaned with acetone or isopropanol (IPA), which means a stronger chemical like and acid may be appropriate, however, for health and safety reasons, this cannot be done outside a fume cupboard. Furthermore, this system is used for Diamond-like carbon (DLC) deposition which has caused an unknown layer of material to be coated on the chamber walls which is easily blown (as dust) when venting the chamber.

Overall, the process was not as reliable as desired for reproducible growth, and Thomas Swan CNTs were used instead.
## Appendix B: Electrical conductivity raw data

Table II-1. Raw data collected using the Van Der Pauw method for measuring the sheet resistance and computing the electrical resistivity from the CNT film thicknesses.

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