CRANFIELD UNIVERSITY

P. G. Krause

Oxidation Resistant Flexible Transparent Conductive Electrodes by Synthesising CuNi Nanowires

School of Aerospace and Manufacturing
Ultra-Precision Engineering

MRes
Academic Year: 2017 - 2018

Supervisor: Dr Zhaorong Huang
Associate Supervisor: Prof Jose Endrino
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This thesis is submitted in partial fulfilment of the requirements for the degree of MRes

ABSTRACT

This research attempts to find a replacement for ITO that is flexible and doesn't oxidise by synthesising CuNi nanowires in a single pot process. Indium is scarce, expensive, and non-flexible so has to be printed on solid substrates such as glass. It involved costly and wasteful processes to apply and cure and is running out. Copper nanowires are a cheap alternative but they oxidise. The simple difference between synthesising Cu NW's and CuNi NW's is the addition of glucose which is low cost. The nickel inhibits oxidation so no extra processes are required to protect them.

Copper-nickel nanowires have rarely been synthesised and this research explains how to and shows that copper-nickel nanowires could directly replace ITO.

This research shows a systematic approach to solving the problem, by varying the glucose and heat cycle to maximise the aspect ratio and achieve a nickel content of 5 > 20%. Once the best nanowires were synthesised, the ink concentration and thickness was varied to optimise the optoelectronic properties.

Many CuNi NW's were grown with >700 aspect ratio and Ni content 5 > 20% by adjusting the glucose content. The aspect ratio increases when the synthesis temperature is lowered as low as 160 °C while maintaining the Ni content range. A compromise is necessary as higher nickel content reduces the aspect ratio. A synthesis of 8.9% Ni was found to be as conductive after 112 days, as it was when it was made, thus showing that CuNi alloy does inhibit oxidation.

This research has shown that CuNi NW's can replace ITO in every area while being over 100 times less expensive and easier to make, apply and cure, enabling more uses of this technology in the future. They are also flexible which will allow even more areas of use.

Keywords: ITO replacement, copper nickel nanowires, low temperature synthesis, one pot synthesis

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Most of all, I wish to thank Dr Quentin Lonne. Without him, this research would not have happened at Cranfield University. It was he that discovered that it was possible to incorporate nickel into copper nanowires during his research at Cranfield University in 2016 to 2017 by the simple addition of glucose. This addition of nickel into the nanowires largely inhibits corrosion and makes copper-nickel nanowires a very serious contender for the replacement of Indium Tin Oxide (ITO) for a transparent conductive layer that modern electronics demands. It was this realisation that has made my research unique. It was also Quentin, that produced the SOP for this work that appears in Appendix A and he also synthesised our first batch of nanowires to demonstrate the process while I took notes. Not only was he there to help me initially get started but has made himself available when required throughout the entire research. He not only helped me with my research but everybody else in Building 70 with their research. He is a brilliant chemist and a very nice person that will be severely missed by Cranfield University when he leaves in November 2018. It has been an honour to work alongside him. This research has occupied my mind almost completely for 5 months but it has been stimulating and exciting for the duration.

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TABLE OF CONTENTS

ABSTRACT i
ACKNOWLEDGEMENTS iii
LIST OF FIGURES x
LIST OF TABLES xii
LIST OF EQUATIONS xiv
LIST OF ABBREVIATIONS xv
1 INTRODUCTION 17
  1.1 Overview 17
  1.2 Aims and Objectives 17
  1.3 Safety using Nanowires 17
  1.4 Notes 17
2 Background, Motivation and Literature Review 18
  2.1 Background and Main Uses 18
    2.1.1 History of Transparent Conductive Electrodes (TCE) 19
    2.1.2 Previous Research on Cu and CuNi Nanowires 19
  2.2 TFC Conductance, Transmittance and Surface Finish 20
  2.3 Conductance vs Oxidation Rate of Copper Nickel Alloys 21
  2.4 Expected Outcomes 22
  2.5 Expected Future Uses 23
  2.6 Key Targets Summary 23
3 SYNTHESIS AND CHARACTERISATION METHODS 25
  3.1 Synthesis 25
    3.1.1 Ingredients 25
    3.1.2 Synthesis Equipment 25
    3.1.3 Synthesis 26
    3.1.4 Cooling 27
    3.1.5 During Synthesis Sampling 27
  3.2 Scrubbing (Cleaning NW's) 29
    3.2.1 Scrubbing Ingredients 29
    3.2.2 Scrubbing Equipment 29
    3.2.3 Scrubbing Process (Cleaning NW's) 29
  3.3 Ink 30
    3.3.1 Ink Ingredients 30
    3.3.2 Ink Procedure 30
  3.4 Thin Film Coating 30
    3.4.1 Coating Equipment 30
    3.4.2 Coating Procedure 31
  3.5 Curing or Fusing 32
    3.5.1 Curing Heat Treatment 32
    3.5.2 Curing UV Treatment 33

3.6 Characterisation 35
3.6.1 Optical Microscope (OM) 35
3.6.2 Scanning Electron Microscope (SEM) 36
3.6.3 Resistance (Four Point Probe) 39
3.6.4 Transmission (Spectrophotometry) 42
3.6.5 XRC using XRD 42
4 PROCESSES, PROCEDURES AND PLAN 44
4.1 Processes 44
4.1.1 CPA 44
4.2 Plan 46
4.2.1 Synthesis, Scrubbing and Heat Treatment Plans 46
4.3 Data Recording 47
4.3.1 Example of typical data in spreadsheet 48
5 RESULTS 50
5.1 Copper-Nickel Nanowire Synthesis 50
5.1.1 High Temperature – Vary Glucose 50
5.1.2 Lower Temperature – Vary Glucose 52
5.1.3 First Aim – Increase Aspect Ratio > 400 55
5.1.4 Second Aim – Optimise Nickel Content 57
5.2 Curing 58
5.2.1 Heat Curing 58
5.2.2 UV Curing 59
5.3 Optoelectronic Testing 60
5.3.1 Inks 60
5.3.2 Resistance Testing 62
5.3.3 Transmission Testing 65
5.4 Crystal Structure XRD 70
5.5 During Synthesis Sampling 71
5.5.1 During Synthesis Sampling Setup 72
5.5.2 During Synthesis Sampling Trial 72
5.5.3 During Synthesis Sampling 75
6 DISCUSSION 82
6.1 Copper-Nickel Nanowire Synthesis 82
6.1.1 High Temperature – Vary Glucose 82
6.1.2 Lower Temperature – Vary Glucose 83
6.1.3 First Aim – Increase Aspect Ratio > 400 84
6.1.4 Second Aim – Optimise Nickel Content 85
6.2 Curing 85
6.2.1 Heat Curing 85
6.2.2 UV Curing 86
6.3 Optoelectronic Testing 86
6.3.1 Inks 86

        6.3.2 Resistance Testing.. 87
        6.3.3 Transmission Testing 89
        6.3.4 Optoelectronic Properties.. 91
    6.4 Crystal Structure XRD.. 92
    6.5 During Synthesis Sampling... 92
        6.5.1 During Synthesis Sampling Setup....................................... 92
        6.5.2 During Synthesis Sampling Trial 93
        6.5.3 During Synthesis Sampling 94
7 CONCLUSIONS.. 97
    7.1 First Aim... 97
    7.2 Second Aim 97
    7.3 Third Aim 98
    7.4 Fourth Aim 99
    7.5 General Conclusions.. 99
8 FUTURE RESEARCH... 100
    8.1 Improving Processes 100
    8.2 Improving Methods 100
REFERENCES... 101
APPENDICES 107
    Appendix A Original SOP... 107
    Appendix B Original CPA Expansion of Processes 111
    Appendix C Revised CPA Outline... 115
    Appendix D Revised CPA Expansion of Processes.......................... 116
    Appendix E Revised SOP 120
    Appendix F Spreadsheet of Data.. 130

LIST OF FIGURES

Figure 1 Nanowire Synthesis.......... 26

Figure 2 During Synthesis Sampling 27

Figure 3 During Synthesis Sampling Extraction 28

Figure 4 Mayer Rod Spreading 31

Figure 5 Mayer Rod Ink Coverage 32

Figure 6 Tubular Oven for Heat Treatment 33

Figure 7 UV Treatment.......... 34

Figure 8 SEM Carousel stub holder 37

Figure 9 Four Terminal Sensing 41

Figure 10 Four Point Probe - Resistance Measurement 41

Figure 11 Critical Path Analysis (CPA) Outline.......... 44

Figure 12 CPA Details Processes 1 to 5 45

Figure 13 Colour Key for CPA 45

Figure 14 Synthesis Time Plan.......... 47

Figure 15 Syntheses 190-195 °C Glucose vs Aspect Ratio 51

Figure 16 Syntheses 190-195 °C Glucose vs Ni Content.......... 52

Figure 17 Temperature Varied - Glucose vs Aspect Ratio 53

Figure 18 Temperature Varied - Glucose vs Nickel Content 55

Figure 19 Aspect Ratio vs Temperature - Glucose 0.75 g.......... 56

Figure 20 Glucose vs Nickel Content - 160 °C 57

Figure 21 OM Micrographs of HT on Glass vs UV on PET for Synthesis 4...... 60

Figure 22 Synthesis 39 Micrograph.......... 61

Figure 23 Ink Dilutions from 40 mg/ml Concentration Ink.......... 61

Figure 24 Resistance 1, 3, 4 & 5 over Time 63

Figure 25 S39 Resistance Deterioration.......... 64

Figure 26 S28 Resistance Deterioration.......... 65

Figure 27 Synthesis 1 on Glass Transmission 66

Figure 28 Synthesis 1 on Glass Transmission with ITO 66

Figure 29 S39 Wavelength vs Transmission – Vary Concentration.................. 67
Figure 30 S39 Wavelength vs Transmission – Vary Average Concentration ... 68
Figure 31 S39 Transmission - Vary Mayer rod.. 68
Figure 32 S28 Transmission.. 69
Figure 33 S5 Transmission.. 69
Figure 34 XRD Pattern of Syntheses 1 to 5 70
Figure 35 XRD Pattern Close Up 70
Figure 36 During Synthesis Sampling 3D Illustration 71
Figure 37 Micrographs of sample 33C 73
Figure 38 Sample 37B Micrograph.. 77
Figure 39 Synthesis 5 NW Micrograph.. 83
Figure 40 Synthesis 5 Micrograph... 88
Figure 41 S5 Cured Slide 91
Figure 42 Synthesis 37A-02 and 37D-02 Micrographs.................................... 95
Figure 43 Original CPA Expansion 1... 111
Figure 44 Original CPA Expansion 2... 112
Figure 45 Original CPA Expansion 3... 113
Figure 46 Original CPA Expansion 4... 114
Figure 47 Revised CPA.. 115
Figure 48 Revised CPA Expansion 1 116
Figure 49 Revised CPA Expansion 2 117
Figure 50 Revised CPA Expansion 3 118
Figure 51 Revised CPA Expansion 4 119

LIST OF TABLES

Table 1 Copper / Nickel Property Comparison [32] 21

Table 2 Comparative Properties of CuNi alloys between 5-20 % Ni [33].......... 22

Table 3 Carousel Position Coordinates 37

Table 4 Example of data in Spreadsheet 48

Table 5 Synthesis 190-195 °C Vary Glucose 50

Table 6 Lower Temperature Aspect Ratio Data 53

Table 7 Lower Temperature Ni Content Data.. 54

Table 8 Glucose Constant at 0.75 g - Vary Temperature 56

Table 9 Temperature 160 °C - Vary Glucose 57

Table 10 Resistance 1, 3, 4 & 5 over Time Data.. 62

Table 11 S39 Resistance Data - Vary Concentration Example 63

Table 12 S39 Data - Resistance Deterioration 64

Table 13 S28 Data - Resistance Deterioration 65

Table 14 Sample 33C NW Aspect Ratio 74

Table 15 Sample 37A Nanoparticle Sizes 76

Table 16 Sample 37A NW Aspect Ratio.. 76

Table 17 Sample 37B NW aspect Ratio 78

Table 18 Sample 37B Nanoparticle Sizes 78

Table 19 Sample 37C Nanowires and Nanoparticles 79

Table 20 Sample 37D NW Aspect Ratio 80

Table 21 Sample 37D Nanoparticles.. 80

Table 22 Growth During Synthesis Summary... 81

Table 23 Aspect Ratio - Vary Temperature 83

Table 24 Ni Content - Vary Temperature 84

Table 25 Increase Nickel Compound 85

Table 26 Optoelectronic Properties Summary... 91

Table 27 Peak Values 92

Table 28 Spreadsheet of Data Part 1 (Repeat of Table 4) 130

Table 29 Spreadsheet of Data Part 2 131

Table 30 Spreadsheet of Data Part 3 132

LIST OF EQUATIONS

$I = V / R$ --- Equation 1 Ohms Law 40

$R = \rho.L/A$ --- Equation 2... 40

$A = w \times t$ --- Equation 3.. 40

$R = \rho.L/W.T$ ---Equation 4 40

$R_s = \rho/T$ --- Equation 5.. 40

$\boldsymbol{Rs = \pi \ln(2) \Delta VI}$ ---Equation 6 [38]... 40

$Rs = 4.53236\ V/I$ --- Equation 7 40

$C_s = C / (V+V_s) = 40 / (1+V_s)$ ---- Equation 8... 87

$V_s = (40 / C_s) -1$ --- Equation 9.. 87

LIST OF ABBREVIATIONS

IT	Information Technology
NP	Nanoparticle
NW	Nanowire
CuNi	Copper-Nickel
TCE	Transparent Conductive Electrode
R2R	Roll-to-Roll
OLED	Organic Light Emitting Diode
ITO	Indium Tin Oxide
PVD	Physical Vapour Deposition
Cu	Copper
Ni	Nickel
Ag	Silver
Au	Gold
MEMS	Microelectromechanical systems
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
MG	Micrograph
TFC	Transparent Flexible Conductor
LH	Left Hand
AU	Arbitrary Unit
RH	Right Hand
XRD	X-Ray Diffraction
EDS	Energy-Dispersive Spectroscopy
OM	Optical Microscope
IR	Infrared
UV	Ultraviolet

1 INTRODUCTION

1.1 Overview

This project will develop and optimise oxidation-resistant Transparent Conductive Electrodes (TCE's) using copper-nickel (CuNi) nanowires (NW's) to replace Indium Tin Oxide (ITO).

1.2 Aims and Objectives

1. Increase aspect ratio of NW's >=400.
2. Control Ni content of CuNi alloy NW (between 5% - 20% Ni).
3. Optimise ink formulation / concentration.
    a. Optimise the optoelectronic properties (resistivity / transparency).
    b. Study and record oxidation resistance and transmission of coated substrates throughout the project.
4. To better understand how anisotropic growth works. (Personal Aim)

1.3 Safety using Nanowires

The full safety effects of working with nanowires have not been fully investigated yet but they are expected to be similar to working with asbestos. The metal nanowires can possibly get inside cells and damage DNA causing cancer and respiratory problems if inhaled. All work involving the synthesis of NW's should be carried out in a laboratory whilst wearing the appropriate lab coat, safety goggles and gloves under a fume hood where possible. Any spilt or waste nanowires should be disposed of by wrapping in paper and placing in a separate zip lock bag that is suitably marked and kept in a special waste area.

The main COSHH assessment was COSHH 699-0518 Synthesis of Copper-Nickel nanowires transparent conductive electrodes (CuNi TCE's).

1.4 Notes

All diagrams, tables, drawings, charts, photographs and micrographs are produced by the author and therefore not referenced.

Blue highlighted words are interactive cross references. Press Ctrl Click to follow.

2 Background, Motivation and Literature Review

2.1 Background and Main Uses

To make modern devices such as touch screens, thin film solar cells [1], light emitting diodes (OLED) [2], thermo-electrics, sensors and displays, TCE's are necessary to provide a conductive but transparent layer. Until recently, most have been made using Indium Tin Oxide (ITO) but this has limitations. Indium is expensive and scarce so the price fluctuates wildly with availability [3]. The process of applying it as a thin film is wasteful and slow as it normally uses Physical Vapour Deposition (PVD). It also requires expensive vacuum equipment. Increasingly, flexibility is becoming a requirement and ITO is brittle and therefore not suitable for this application [4]. After a few bending cycles it forms micro cracks which considerably reduces its electrical conductivity.

Worldwide research is addressing this problem by focusing on alternative materials such as, graphene [4], carbon Nanotubes [5], poly(3,4-ethylenedioxythiophene poly(styrenesulfonate) (PEDOT:PSS) [6,7], silver Nanowires [2,8], copper Nanowires [3,9] and zinc oxide [10] based transparent conducting oxides etc. However, graphene and carbon nanotubes have poor optoelectronic performance compared with ITO [11]. Noble metals exhibit superior conductivity and transmittance, but availability and price fluctuation make them uncompetitive for large area coverage. Silver NW's can achieve better transparency and lower sheet resistance (Rs) than ITO and can be deposited on flexible substrates but uses vacuum transfer or spin coating that increases an already high cost [12].

Because of coppers abundance, availability, comparative low cost and high electrical conductivity, copper Nanowires are the most promising alternative available so much research is concentrating in this area [13–15]. Cu NW's can be fabricated by low cost, large scale wet chemical synthesis and deposited by low cost high speed processes and is particularly suited to Roll-to-Roll (R2R) [4]. It is also very flexible allowing thousands of bending cycles without significant deterioration [3,9,16]. Copper is 1000 times more abundant than silver but only

6% less conductive. It is 100 times cheaper than Ag or ITO and cheaper and less wasteful to deposit.

2.1.1 History of Transparent Conductive Electrodes (TCE)

The first recorded TCE's were made from SnO_2: Sb by spray pyrolysis in 1947 [37]. The first recorded use of ITO (In_2O_3Sn) was done also using spray pyrolysis in 1951 [37]. By 1955 ITO was applied by sputtering [37] but it wasn't applied by CVD until the late 1960's. The process has been used continuously since the start but it wasn't until 2007 that it really took off and expanded with the launch of the Apple I-phone.

2.1.2 Previous Research on Cu and CuNi Nanowires

This research concentrates on replacing ITO with CuNi nanowires as Cu is conductive, relatively cheap, flexible and freely available. Integrating Ni into the nanowires should provide oxidation resistance, making it a serious contender.

A review paper from 2016 was found that looks specifically at copper nanowires and their applications by Nam, V et al. [17]. This obviously proved very useful, gathering relevant information into one place and providing 91 other relevant reference papers in the process.

It seems that Cu NW are the perfect alternative to ITO but it does have one serious drawback; it is prone to oxidation under ambient conditions but especially in hot or challenging environments.

Preventing the oxidation of Cu NW's is the main remaining obstacle to be overcome. In a paper by Xue, J et al. [26] they found that by coating Cu NW's with a CuNi coating (CU@CuNi), they could increase the oxidation resistance of the NW coating by up to 900 times while not reducing the transmission, 92% to 85% at 30 Ω/sq) significantly. In this research, oleylamine was used as a capping agent, reducing agent, solvent and surfactant.

Very few other research papers investigating the manufacture of CuNi alloy NW's could be found [19–26]. However, [19] is only working with Ni and NiO, [20] is non-transparent CuNi, [23] is Cu NW with a Ni coat, [21,22,24,26] are all Cu NW's but with a CuNi alloy coat. Only [25] is growing CuNi alloy NW's but for optical properties rather than TCE's. Only one research project that synthesised uncoated CuNi alloy NW's in a one pot process for TCE's was found. This was a conference presentation at the ECNF2016 at Bilbao, Spain on 19-21 October 2016 by Lonne, Q [27]. The main purpose of this research project was to grow Cu NW's in a one pot synthesis process, curing them with UV treatment, rather than heat treatment [32]. This research also used oleylamine as a capping agent, reducing agent, solvent and surfactant to synthesise Cu NW's. However, towards the end of this research it was found that by the addition of glucose, some of the Ni compound would be incorporated into the NW's rather than purely acting as a catalyst.

A review paper, "Oleylamine in Nanoparticle Synthesis" by Mourdikoudis, S. et al [28] in 2013, concentrates on the use of oleylamine, rather than other alkylamines, for the synthesis of nanostructures such as nanoparticles and nanowires. This review commented that it is not possible to obtain oleylamine at purities higher than 85-90% which may cause some inconsistencies, according to what the impurities are.

Glucose was used by Li, S. [18] in 2014 to reduce the cost of producing Cu NW's on a large scale using a pressure cooker. They used dual capping agents, oleylamine and oleic acid. Glucose was used as a reducing agent.

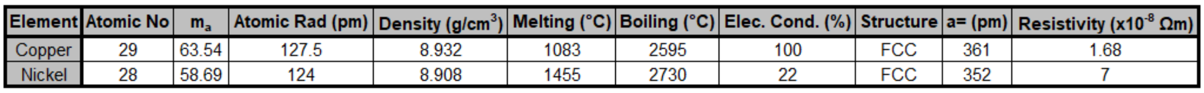
2.2 TFC Conductance, Transmittance and Surface Finish

For ideal performance a Transparent Flexible Conductor (TFC) should be highly conducting while being as transparent as possible. In addition, as high roughness of the film surface can lead to short circuits and leakage, the surface roughness should be minimised [29,35].

According to Nam.V, [17] conductivity is proportional to the film thickness, the thicker the film the higher the conductivity. However, the thicker the film the lower the transmittance. This leads to a compromise between conductivity and transmittance. Additionally, the thicker the nanowires the lower the resistance so the greater the conductance. At best, the surface roughness will be twice the thickness of the nanowire diameters because they must overlap and fuse to form a conductive film mesh layer (percolation) [30]. A NW is one dimensional (1D) and the surface covered is two dimensional (2D). Therefore, if a NW is twice as long, only a quarter of the number density of nanowires will be required to achieve percolation (inverse square law). This means that NW's should be thinner and longer to achieve better transmittance [31]. Additionally, the surface roughness will decrease by twice the diameter of the nanowire. Conversely, thinner NW's will have a higher individual resistance and so be less conductive but will transmit more light. However, with good percolation and aspect ratio, the diameter of individual NW's will not relate to the conductivity of the conductive film but it will alter the transmittance, therefore small diameter, good aspect ratio NW's are highly desirable.

2.3 Conductance vs Oxidation Rate of Copper Nickel Alloys

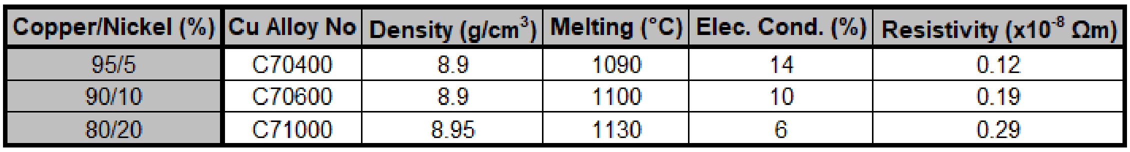
Copper with atomic number 29 and an atomic mass of 63.54 and atomic radius of 1.275 x 10^{-10} m is a Face Centred Cubic (FCC) with sides, a = 0.3608 nm, a density of 8.932 g/cm^3 @20°C, an electrical conductivity of 100% (reference) and a resistivity of 0.017241 Ωmm^2/m @20°C. Its melting point is 1083°C and boiling point 2595°C [32]. When impurities are added to copper it always loses conductivity. It is proposed to synthesis CuNi NW's so it is necessary to look at the properties of Ni compared with Cu.



Element	Atomic No	m_a	Atomic Rad (pm)	Density (g/cm^3)	Melting (°C)	Boiling (°C)	Elec. Cond. (%)	Structure	a= (pm)	Resistivity (x10^{-8} Ωm)
Copper	29	63.54	127.5	8.932	1083	2595	100	FCC	361	1.68
Nickel	28	58.69	124	8.908	1455	2730	22	FCC	352	7

Table 1 Copper / Nickel Property Comparison [32]

Table 1 shows comparisons between copper and nickel properties. They are both similar sized face centred cubic's with similar density. Nickel has a higher melting temperature (1455 °C) compared to Copper (1083 °C) so it can be expected that the higher the Ni content the greater the temperature that fusion of the NW will take place. The biggest difference between them is the electrical conductivity. If Cu is considered to be 100% conductive, Ni is only 22% conductive. It is therefore expected that the Ni % will need to be minimised while keeping enough to still being capable of inhibiting oxidation sufficiently.



Copper/Nickel (%)	Cu Alloy No	Density (g/cm^3)	Melting (°C)	Elec. Cond. (%)	Resistivity (x10^{-8} Ωm)
95/5	C70400	8.9	1090	14	0.12
90/10	C70600	8.9	1100	10	0.19
80/20	C71000	8.95	1130	6	0.29

Table 2 Comparative Properties of CuNi alloys between 5-20 % Ni [33]

Table 2 compares properties of copper-nickel alloys containing between 5 and 20% nickel. The electrical conductivity of all three alloys are less than both Cu and Ni when in their elementary states. This may be influenced by small additional content of other elements (Fe, Mn) allowed in the definition of official Cu alloy numbers. It is hoped and expected that when they are not present, the percentages will be higher, within the range of the two elements (22 - 100 %).

2.4 Expected Outcomes

This proposed research will continue the findings of Lonne.Q at Cranfield University in 2016 [34] where the addition of glucose incorporates Ni into the NW's as a CuNi alloy. As the aspect ratio is reduced when Ni is incorporated, the first aim is to increase it back to >400. The second aim is to control the Ni content of NW's to between 5 and 20%. This percentage should be kept to a minimum because the Ni content adversely affects the aspect ratio and therefore the optoelectronic properties. However, it must be high enough to inhibit oxidation. Once reliable NW's have been produced that satisfy the first two aims, the ink concentrations and formulation will be optimised for the best optoelectronic properties.

The unique aspect of this research is the addition of glucose to synthesis copper nickel alloy nanowires that do not oxidise.

During this research, the conductivity and transparency will be regularly checked throughout the project to check for any oxidation.

The best possible outcome of this research is to be able to synthesis oxidation resistant nanowires with good enough optoelectronic properties to be a genuine replacement of ITO.

2.5 Expected Future Uses

It is also expected that TCE will become more widespread once a cheaper and simpler alternative to ITO is found. It can be expected to be used in new areas such as induction shielding, minimising the generation of static electricity, minimising radio frequency interference and anti-fog for windows. Reduced costs will also make it possible to turn glass windows into flat screen displays with touch screen capability. Basically, being able to print a computer onto a desired surface using thin film batteries and thin film solar cells as a power source. Being able to print nano-electronics onto flexible substrates using R2R will also enable the use of smart packaging etc.

2.6 Key Targets Summary

The main target of this research is to synthesise copper-nickel alloy nanowires that are transparent and conductive enough to replace Indium Tin Oxide.

1. The main challenge to overcome to achieve this target is that when nickel is included into the wires to inhibit oxidation, the aspect ratio goes down. That is why the first aim (Increase aspect ratio of NW's >=400.) is to improve the aspect ratio as high as possible which is key for good percolation which will increase conductivity while remaining optically transparent.
2. To inhibit oxidation of the nanowires they should contain between 5 and 20% nickel. The higher the nickel content, the lower the aspect ratio so the nickel content should be kept to a minimum. This is why the second aim (Control Ni content of CuNi alloy NW (between 5% - 20% Ni).) is to keep the nickel content high enough to inhibit oxidation but low enough to enable a high aspect ratio. So aims 1 and 2 are inextricably linked and require a compromise.
3. Once aims 1 and 2 have been satisfied and high aspect ratio CuNi NW;s have been synthesised, they can be used to prepare different concentrations of inks which are spread in varying thicknesses so as to achieve the optimum optoelectronic properties. This is the first part of the third aim (Optimise the optoelectronic properties (resistivity /

transparency).) But however good these characteristics are, it must be shown that they will not deteriorate over time by oxidation. The nanowires must not oxidise over the expected lifetime of the surface. This is why the second part of the third aim is to (Study and record oxidation resistance and transmission of coated substrates throughout the project.). Because I do not expect to synthesise the best NW's until close to the end of the project, less optimum syntheses should be monitored from early on as soon as one is found that satisfies aims 1 and 2.

4. The fourth aim (To better understand how anisotropic growth works. (Personal Aim)) is the author's personal aim. If a key target is achieved by chance early on in research, then it will be known how to repeat and achieve the same result again. However, if an understanding is gained then it should be possible to synthesise greater variations of desired results by design at the same time as adding to the overall knowledge of people.

These key target numbers coincide with the Aims and Objectives shown in section 1.2 but add a little more explanation summarising the main purpose and targets of this research.

3 SYNTHESIS AND CHARACTERISATION METHODS

There are many processes for growing nanowires (NW's) to be used as TCE's, which can be loosely grouped into several sub-headings; Synthesis, Scrubbing, Ink, Thin film coating, Curing or fusing and Characterisation or testing.

3.1 Synthesis

There are several ways to grow NW's, but this research will investigate using a single flask wet chemistry method. Some of the chemical ingredient quantities will be varied and the temperature profile altered to try to achieve the optimum aspect ratio, nickel content and optoelectronic properties. Nanoparticles will be grown from scratch as part of the synthesis rather than added during synthesis. The method described here describes the first synthesis made that all others can be compared to.

3.1.1 Ingredients

0.4092 g (2.4 mmol) of copper II chloride dihydrate ($CuCl_2.2H_2O$)

0.2986 g (1.2 mmol) of nickel II acetate tetrahydrate (Ni $(C_2H_3O_2)_2.4H_2O$)

0.50 g (1.4-5.6 mmol) of glucose ($C_6H_{12}O_6$)

25 mL of oleylamine ($C_{18}H_{37}N$)

Acetone (for cleaning) ($(CH_3)_2CO$)

3.1.2 Synthesis Equipment

50 cl round bottom flask

Cork holder

Scales, measuring tube and spatula

Magnetic stirrer

Magnetic stirring hotplate (model 3810000 RCT basic IKAMAG, IKA)

Reflux column with a top in-line oil bubbler

Water and N_2 supply

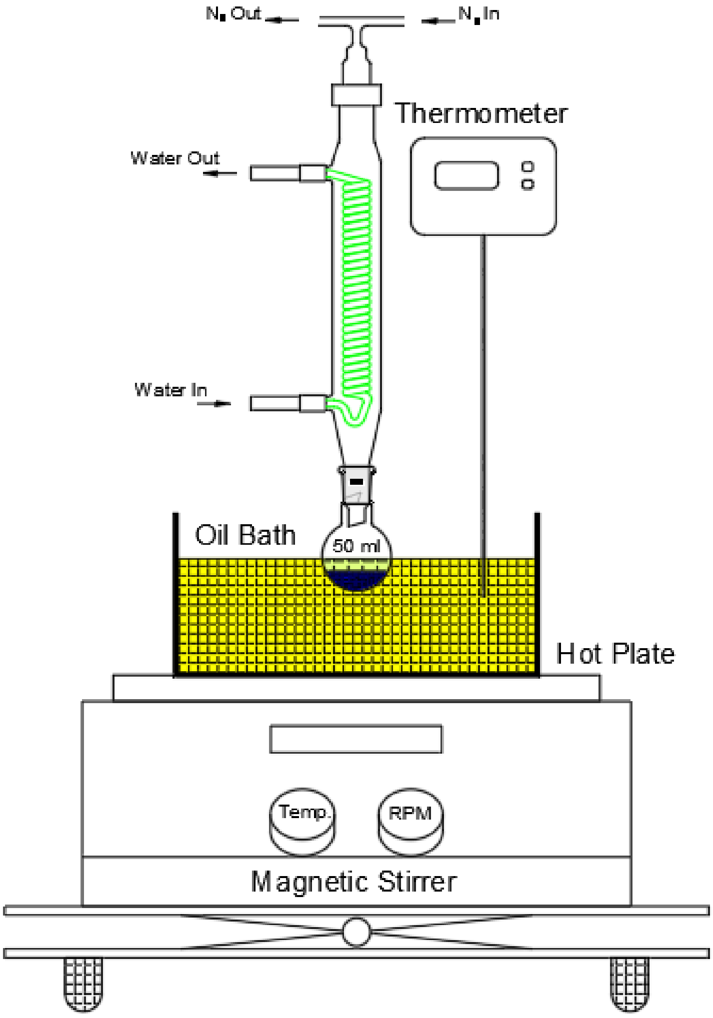


Figure 1 Nanowire Synthesis

Figure 1 shows the synthesis setup. Magnetic stirrers are placed in the 50 ml flask and in the oil bath to ensure good mixing and consistent heat.

3.1.3 Synthesis

The ingredients were measured and placed into the 50 ml round bottom flask sitting in the cork holder, the magnetic stirrer added, then placed under the reflux column. The oil bath was raised so as to just cover the solution level, the water and N_2 supply turned on low through the reflux column. Heat the solution to 95 °C for 30 minutes with the stirrer set to 800 rpm to remove 0_2(g) and water traces. The solution remains blue until the temperature is turned up to 195 °C to reduce the Cu and Ni and form CuNi nanoparticle seeds. The solution turns dark brown according to the Ni and glucose content. Keep stirring once the temperature is reached for 30 minutes before switching off the stirrer. Keep the solution at 195 °C for 15 - 18 hours while the NW's grow.

3.1.4 Cooling

Stop the heating and let the solution cool down naturally with the water and N_2 still flowing. Wash all the equipment thoroughly. As the Oleylamine is so viscous, especially when combined with cooked glucose, it is best to start the scrubbing process immediately when the solution has cooled to between 50 – 60 °C, initially using warmed hexane (50 °C). This is because the melting point of oleylamine is only 21 °C and is much more viscous when cold.

3.1.5 During Synthesis Sampling

To try to better understand the synthesis process, the setup was changed to allow during synthesis sampling.

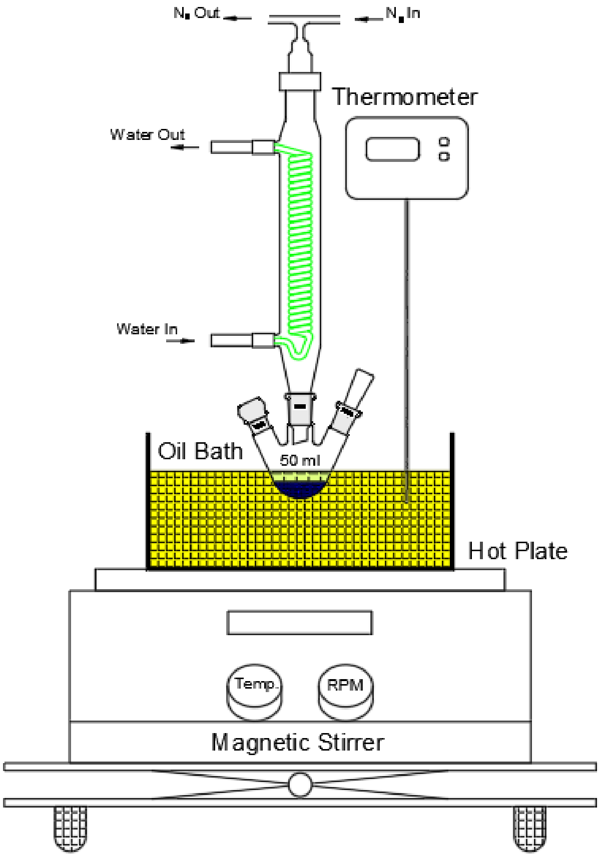


Figure 2 During Synthesis Sampling

Figure 2 shows how the setup was changed for during synthesis sampling. The setup is almost identical to normal synthesis except that the 50 ml round flask is replaced with a 50 ml round flask that has at least two entries. I only had a three-way flask available, so I blocked the third entry off with a glass stop. A rubber septum is fitted to the second entry to allow a syringe to be inserted through the rubber to extract a sample during synthesis without allowing air into the system.

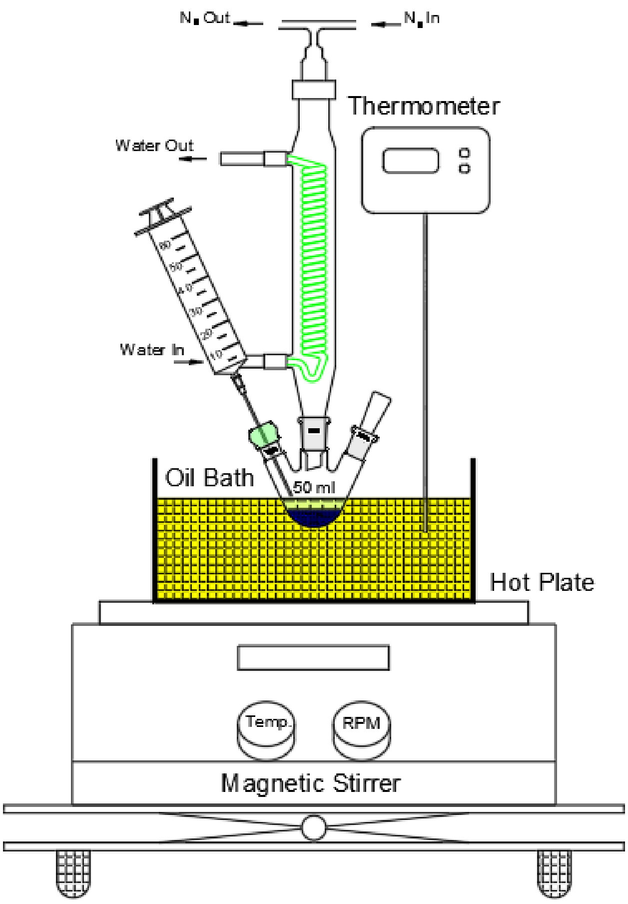


Figure 3 During Synthesis Sampling Extraction

Figure 3 shows the sample being taken by insertion of the syringe through the septum. Once the temperature is increased to synthesis temperature, a syringe can be inserted through the septum to extract a sample during synthesis, without allowing ambient air into the flask.

3.2 Scrubbing (Cleaning NW's)

The synthesised CuNi NW's will need a thorough cleaning to remove the organics and other ingredients before they can be mixed with a suitable ink.

3.2.1 Scrubbing Ingredients

Anhydrous Hexane (C_6H_{14})

Acetic acid ($C_2H_4O_2$)

Isopropyl alcohol IPA (C_3H_8O)

3.2.2 Scrubbing Equipment

2x 50 ml bottle adapted for centrifuge

Centrifuge model AccuSpin 400 Fisher Scientific

Vortex model Topmix FB15024 Fisher Scientific

3.2.3 Scrubbing Process (Cleaning NW's)

The NW solution was transferred to one of the 50 ml bottles where warm hexane was added to a total of around 40 ml. This bottle with contents were weighed and the other 50 ml bottle filled with water to the same weight as a counter balance for the centrifuge. Vortex the NW solution in manual mode at about 10 Hz for 2 minutes, then centrifuge for 20 minutes until the NW's have settled to the bottom of the bottle. Remove the supernatant very carefully with a pipette so as not to remove any NW's. Refill with warm Hexane to about 40 ml, weigh and prepare the same weight in the water bottle for counterbalance.

Repeat the vortex / centrifuge process at least;

- 3 times (total) with warm Hexane
- 2 times with isopropyl alcohol (IPA)
- 1 time with acetic acid
- 3 times with IPA

If the removed solution is not clear, repeat the vortex / centrifuge process 1 more time with acetic acid and 3 more times with IPA. When using the hexane, it is necessary to centrifuge the solution for 20 minutes, but the other cleaning fluids only require between 2 to 5 minutes each.

Weigh accurately a 20 ml vial with lid before transferring the NW’s into it and adding around 10 ml IPA. Allow the IPA to evaporate at room temperature so as not to congeal. When dry, weigh the vial with NW’s and lid again and subtract the weight of the empty vial and lid to obtain the total weight of dry NW’s.

3.3 Ink

The ink is designed to stop the NW’s from forming conglomerates and dry quickly when applied as a thin film, but not too quickly. The concentration of NW’s (mg) to ink (ml) can be varied to obtain the optimum optoelectronic properties.

3.3.1 Ink Ingredients

Isopropyl alcohol IPA (C_3H_8O)

Polyvinylpyrrolidone (PVP) $(C_6H_9NO)_n$, 10000 g/mol

Ethyl acetate ($C_4H_8O_2$)

3.3.2 Ink Procedure

Mix 10 ml of IPA containing 0.5 wt% of PVP to 26 vol% ethyl acetate. Add the ink to the dry NW’s to obtain the desired concentration (initially 40 mg/ml). Vortex for 30 minutes at 10 Hz before storage.

Always vortex for 30 – 180 minutes before use so the NW’s are thoroughly mixed into the ink solution. The ink solution is clear and only coloured by the NW’s when shaken like a Christmas snow scene.

3.4 Thin Film Coating

Again, there are many ways to apply the thin film ink coating, but in this research a Mayer rod was used to evenly spread the ink over, either glass or PET film.

3.4.1 Coating Equipment

Glass work surface

Mayer rods (Dyne Testing), 3 grades;

-	#4	wire Ø0.1 mm	forms 10.2 µm wet film
-	#8	wire Ø0.2 mm	forms 20.3 µm wet film
-	#12	wire Ø0.3 mm	forms 30.5 µm wet film

Medium 1 PET $(C_{10}H_8O_4)_n$, 125 ± 25 µm thick

Medium 2 Glass optical microscope slide cut down to 15 mm x 75 mm

3.4.2 Coating Procedure

Using a pipette, form a liquid line parallel to the top edge of the substrate medium. Quickly spread the ink over the medium using the appropriate Mayer rod. Evaporate at room temperature. Repeat for the other two Mayer rods. Once dry, these slides should only be covering the medium by about two NW diameters thick coating of interlocking NW's that are not fused together. A tiny drop of ink can be placed on another slide for viewing under an optical microscope once dry to see if there is good percolation (the NW's overlap each other forming an even coating on the slide once dry). The longer the NW's and the better the aspect ratio, the better will be the conduction when cured and fused together.

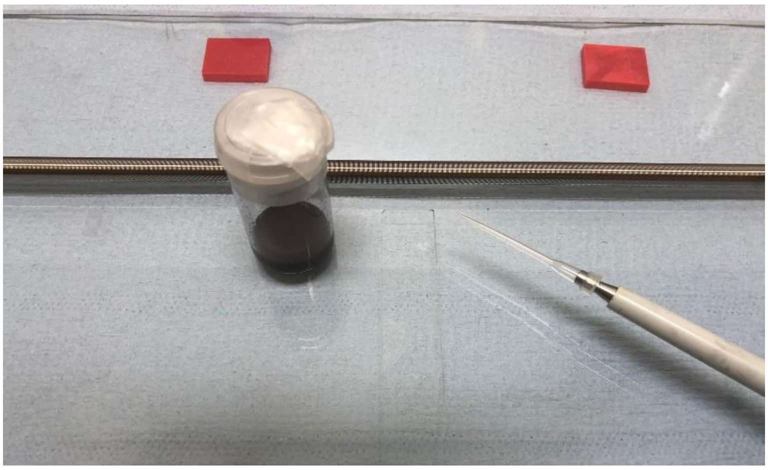


Figure 4 Mayer Rod Spreading

The glass slide and glass is cleaned, the slide wrung to the glass by placing a couple of small drops on the back of the slide and twisting onto the glass to remove any air so that it sticks firm to the glass and does not move when the Mayer rod spreads the ink line placed at the top of the slide with the micro pipette.

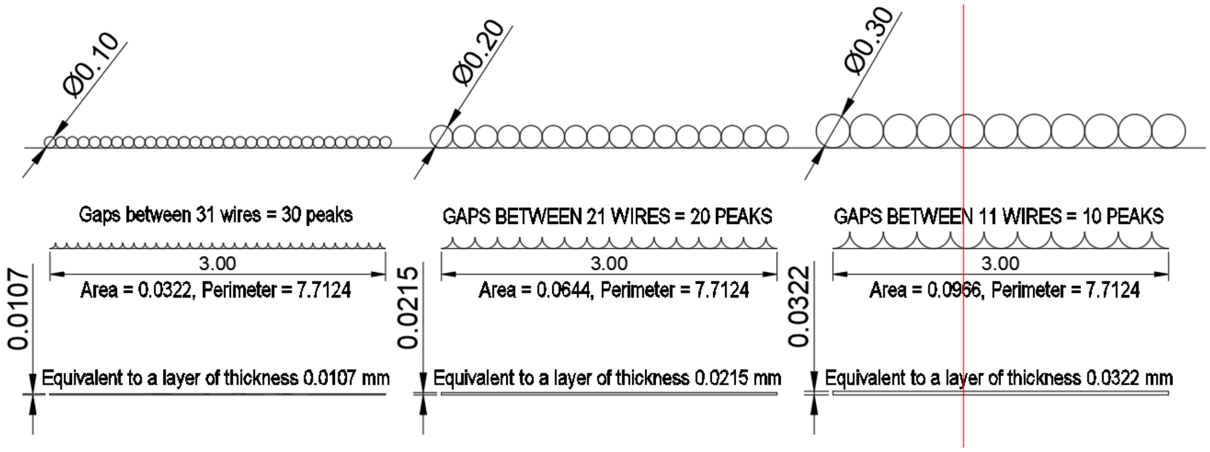


Figure 5 Mayer Rod Ink Coverage

The thicker the wire wound onto the Mayer rod, the thicker the film coat left on the substrate. This is because there is more space between the windings when the wire is thicker. From Figure 5, the diameter 0.1 mm wire (#4 Mayer rod) produces a film of around 10 µm (0.0107 mm) but the 0.3 mm wire (#12 Mayer rod) produces a film of around 30 µm (0.0322 mm).

3.5 Curing or Fusing

Two methods were used in this research, Heat treatment in a tubular oven and ultraviolet treatment (UV). The heat treatment is only suitable for the glass slides as the temperature required to fuse the NW's (350 °C) is above the PET melting temperature (245 °C). Both slide types can be cured using the UV treatment. Both methods need to remove any traces of organic residues prior to fusing the NW's together.

3.5.1 Curing Heat Treatment

When heat treatment is used to cure and fuse Cu NW's, it is done under an inert gas such as N_2 or reducing gas such as Argon with 5% H_2 so that the copper doesn't oxidise as the temperature rises. With CuNi NW's, when the heat treatment is done, the Ni content is unknown, so the same process must be followed.

3.5.1.1 Heat Treatment Equipment

Tubular Oven (model MTF 10/25/130 Carbolite)

3.5.1.2 Heat Treatment Procedure

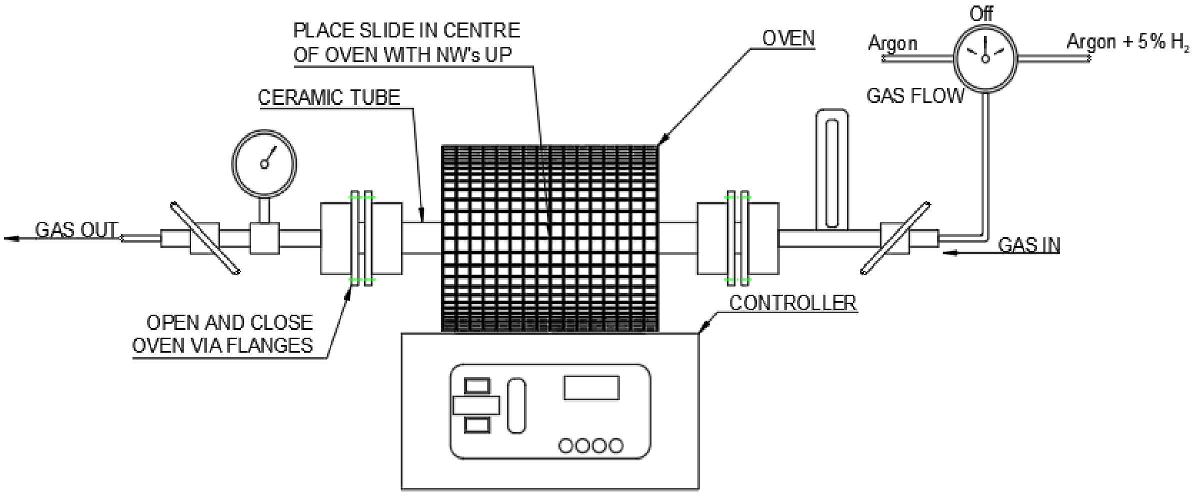


Figure 6 Tubular Oven for Heat Treatment

Figure 6 shows the tubular oven setup. The reason that the glass optical slide has to be cut to 15 mm wide is to fit inside the ceramic tubular oven to cure. Place the slide, NW side up in the centre of the oven and connect to a gas supply of Argon with 5% hydrogen. Leave to purge the Oxygen for one hour before switching power on and adjusting temperature to 380 °C which ensures 350 °C inside the oven. Once up to temperature, hold for 3 hours. Switch heat off and cool down naturally to ambient temperature. Change the gas supply over to pure Argon and purge for 10 minutes before switching off and opening to remove slide with cured NW’s. This is to ensure that hydrogen is not purged into the room when removing the glass slide.

3.5.2 Curing UV Treatment

The UV curing box should always be used inside a fume cupboard because Ozone (O_3) may be produced during the curing process. UV frequencies are dangerous to our eyes, so every effort should be taken to ensure that the light does not escape during warm up and exposure. Metal sticky tape has been used as a light seal around the box and must not be removed.

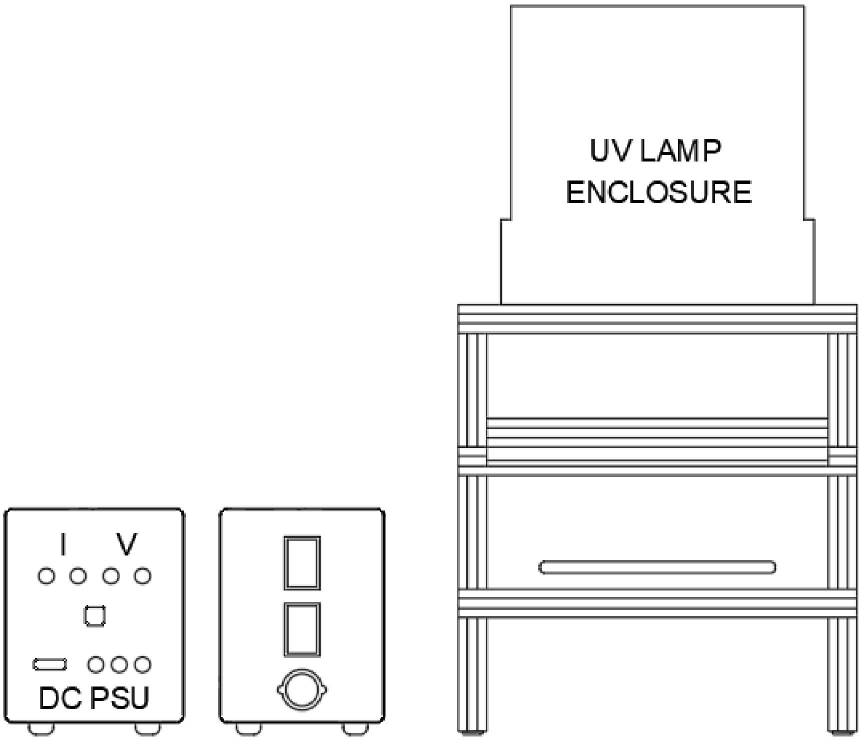


Figure 7 UV Treatment

3.5.2.1 UV Equipment

UV Lamp 430 W (model UVASPOT 400T) Honle fitted with H type mercury vapour bulb (UV 400 H/2).

3.5.2.2 UV Procedure

Put the equipment under a fumed hood. Switch on light for 10 minutes to warm up before inserting slides on exposing platform. Pull aluminium plate out to expose the slide or slides. Time the exposure, closing the aluminium plate after exposure time. The first slide should be exposed for two minutes at a time and tested for conductance following each exposure. This should be repeated while the conductance rose and then fell again so that the optimum exposure time could be found giving the highest conductance. The slide should then be dipped in acetic acid for 10 minutes before air drying and measuring the conductance again. The distance between the lamp and sample is 30 mm.

3.6 Characterisation

There are many measurements and tests that could be performed on the thin film of NW's, but the main ones used in this research are using, optical microscope, Scanning Electron Microscope (SEM), XRD, resistance and transmission.

3.6.1 Optical Microscope (OM)

Two optical Microscopes (OM's) where used during this research.

3.6.1.1 OM Equipment

Binocular optical microscope – Olympus BHL with lenses, x5, x10, x20, x40.

Digital transmission / reflection microscope – Leica EC3 with software LAS Core V4.8. Lenses available, x5, x10, x20, and x40.

3.6.1.2 OM Procedures

The manual binocular OM is close to the laboratory where the synthesis was done so it was convenient to have a look if the percolation was suitable before heat treatments etc. If micrographs were required, then the digital OM was used.

3.6.1.2.1 Binocular OM

Very simple operation, just place the sample under the microscope, switch on and adjust the focus until the NW's could be seen. There are 4 lenses mounted on the viewing column so different magnifications can be tried. It is normally better to find the focus with a low magnification of maybe x5 first, before increasing the magnification. Only small adjustments are required once the sample is in focus when changing the lens.

3.6.1.2.2 Digital OM

Again, very simple operation and similar to the binocular OM except that any desired images can be digitally saved if required. As the transmission OM transmits light through the sample it suited the NW samples better because of their nature but others were available.

3.6.2 Scanning Electron Microscope (SEM)

Three Scanning Electron Microscopes (SEM's) were used during this research.

3.6.2.1 SEM Equipment

SEM XL30 SFEG fitted with Oxford Instruments (EDS) Energy Dispersive Spectroscopy Link Pentafet instrument. Aztec software used V2.2. Cranfield Building 31.

Environmental SEM XL30 ESEM fitted with Oxford Instruments XMax EDS. Aztec software used V2.2. Max resolution 3.5 nm. Cranfield Building 31.

Cold Field Emission SEM – Hitachi S5500. Max resolution 0.2 nm. Cavendish Laboratories University of Cambridge.

3.6.2.2 SEM Procedures

Initially, the SEM XL30 shown in section 3.6.2.2.1 was used to categorise the NW's for length, diameter and Ni content but this machine broke down on 23 April 2018 following synthesis 6 so the Environmental SEM shown in section 3.6.2.2.2 was used but the quality of the micrographs was poor which may have produced unreliable aspect ratio's. Once it became apparent that the SEM XL30 would not be mended imminently, negotiations were made with Cambridge University to use their cold field emission SEM shown in section 3.6.2.2.3 which has a maximum resolution of 0.2 nm. All micrographs for new syntheses were taken at Cambridge until the end of the project and Nickel content on the environmental SEM until the SEM XL30 was fixed in July. Some old syntheses micrographs were redone at Cambridge when the aspect ratio was thought to be suspect.

3.6.2.2.1 SEM XL30 SFEG SEM Procedure

The sample first requires cutting to size. The SEM sample size was kept to a maximum of around 15 mm x 15 mm square. Either the single sample holder can be fitted or the multiple sample carousel which holds up to 7 samples simultaneously. As it takes considerable time to evacuate the air from the sample chamber, if many samples are to be characterised at once, it is worth using. The carousel is numbered so note which sample is placed at which number before evacuating the chamber. Figure 8 below shows the carousel and Table 3 shows the coordinates of each sample position.

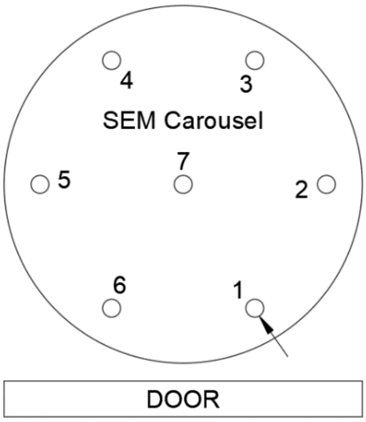
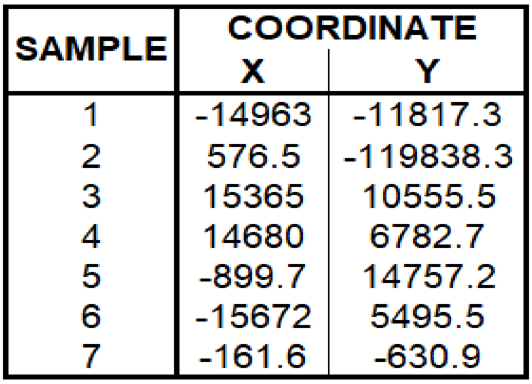


Figure 8 SEM Carousel stub holder

There are 6 possible places to place samples, plus one in the centre, so that the chamber does not have to be vented and re-evacuated between samples. To allow the viewer to know which sample they are looking at, make a note of which sample is in which numbered position then set the coordinates of the position and the SEM will position itself over the centre of the stub required.



SAMPLE	COORDINATE	
	X	Y
1	-14963	-11817.3
2	576.5	-119838.3
3	15365	10555.5
4	14680	6782.7
5	-899.7	14757.2
6	-15672	5495.5
7	-161.6	-630.9

Table 3 Carousel Position Coordinates

Each sample requires sputter coating with a conductive thin film prior to being examined. A thin gold film is normally used to make the samples conductive. Once the chamber has been closed, evacuate to a vacuum of 1.3 x 10^{-4} mbar which takes around 4-5 minutes.

Apply settings for spot size and acc. Voltage. Switch detectors to secondary electrons. Set the beam to between 5-20 kV for image (normally 20 kV). Spot size is normally 5 for composition and higher for high magnification. Set aperture size to 6 for image or 5 for analyse. If only one sample is used set position to 0,0 for centre of sample otherwise to the position of the sample to be examined.

Once the vacuum is OK turn the beam on to 20 kV.

Focus first (right mouse button to focus). Turn contrast down, adjust brightness. To increase magnification, use big dial for course or little for fine or pull-down mouse, alternatively use ± keys. To correct for stigmatism – use mouse back and forward – OK. Working Distance WD needs to be <= 10.

When the desired image has been obtained, select F2 to “scan slow” and save. Repeat for other images and samples.

3.6.2.2.2 Environmental SEM Procedure

The environmental SEM EDS was used to find the nickel content throughout the project from synthesis 7 onwards. Only a single sample holder is available for the environmental SEM but the evacuation time is shorter than for the XL30. A similar sample size of 15 mm square was used when using glass and having them gold sputter coated before use. Once the cold field emission SEM at Cambridge started being used, which demanded a sample size of less than 5 mm x 7 mm x 1mm thick a silicon slice which is already conductive was used, so no gold sputter coating was required.

Open Aztek on the LH computer. Procedures are similar to above in section 3.6.2.2.1 but the EDS column must first be moved to the out position. Set the working distance WD to 6. Set Mag – HR – EDX mode – redo parameters. Select the image required, adjust the contrast/brightness and stigmatism if required and acquire spectra. A larger spot size is required when using EDS to increase the intensity. Select only elements that are required, in our case only Ni and Cu, switching others off. Repeat for at least three positions and save to a spreadsheet on the LH computer. When a spectrum of elements is required focusing properly is not as important as when you are analysing aspect ratios as long as a dense area of NW’s is chosen to fill the screen to minimise the silicon background etc.

3.6.2.2.3 Cold Field Emission SEM – Hitachi S5500

Although this SEM has a resolution of 0.2 nm, it comes at a cost, only one sample of maximum size 5 mm x 7 mm x 1 mm thick can be viewed at once. However, because the sample chamber is so small it doesn't take a long time to evacuate. These samples are metal NW's on a silicon slice which is conductive, so no coating is required. The chamber is evacuated, and the sample holder removed. The silicon sample is placed and held in the sample holder and inserted back into the SEM. Follow the instructions on the front of the SEM adjacent to where the sample holder is inserted, to both remove and insert the holder. Once the chamber has been evacuated, set the voltage to 20 kV.

Prior to using this SEM liquid nitrogen must be placed inside the SEM to condense any water vapour inside the column so as to achieve a higher vacuum. Wait a short time for the temperature to equalise otherwise your image may drift.

Again, the procedures are similar to adjust the stigmatism, contrast, brightness and focus. Set the magnification to the desired amount and frame your specimen, focus and slow scan an image remembering to save this image each time. Repeat for enough images to estimate the average diameters and lengths of NW's before changing the sample. At least 3 high magnification images (500 nm – 5 µm) were taken to estimate the diameters and 3 lower magnification out the lengths (30 µm - 100 µm).

3.6.3 Resistance (Four Point Probe)

3.6.3.1 Resistance Equipment

DC Current Injection – G & E Bradley Ltd. Calibrator type 132

Digital Multi-meter – Keighley 195 A DMM

Four point probe – model 3007A, Kulicke & Soffa

3.6.3.2 Four Point Probe – Sheet Resistance Theory

Resistance of conductors are normally measured between two points. The properties of the material determine how conductive the material is. If a potential difference or voltage (V) is between the two points of measurement, a current (I) flows between these two points. The relationship between the voltage (V) applied, the current (I) that flows and the resistance (R) of the material is governed by Ohms Law.

$I = V / R$ --- Equation 1 Ohms Law

The larger the cross sectional area of the conductor, the lower the resistance. The greater the distance of measurement l the larger the resistance.

$R = \rho.L/A$ --- Equation 2

Where R = resistance in Ω, ρ = resistivity of material in Ω.m, L = length in m and A = Area in m^2. The area A can be broken down as; -

$A = w \text{ x } t$ --- Equation 3

Where W = width in m and T = thickness in m. Substitute Equation 3 in Equation 2.

$R = \rho.L/W.T$ ---Equation 4

Consider a square of the conductive thin film measured between terminals 1 and 4 (see Figure 9) where L = W, they will cancel out in Equation 4 leaving; -

$R_s = \rho/T$ --- Equation 5

Where R_s is the square sheet resistance measured in Ω/□.

A conductive thin film can be considered to have zero thickness T and by some mathematical wizardry; -

$$Rs = \frac{\pi}{\ln(2)} \frac{\Delta V}{I}$$ **---Equation 6 [38]**

Where distances between the probe terminals 1 to 4 (see Figure 9) are equal (s) and thickness of conductive thin film is no more than 40% of this distance s. Equation 5 is similar to Ohms Law (Equation 1) with the addition of a multiplication factor π/ln(2) which when evaluated equals 4.53236 to 5 dp.

Equation 6 can be replaced by;-

$Rs = 4.53236\ V/I$ --- Equation 7

The 4 point probe is used to inject a stepped variable current in mA and the voltage is measured at each step in mV and Equation 7 is used to obtain the sheet resistance in Ω/□.

The conductivity of the material is inversely proportional to the resistance so a low resistance equals high conductivity.

3.6.3.2.1 Four Terminal Sensing

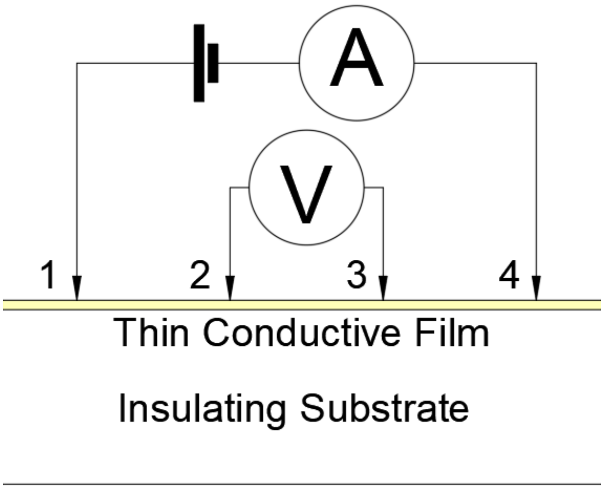


Figure 9 Four Terminal Sensing

Four terminal sensing is more accurate than the normal two terminal sensing and is ideal for measuring conductive thin films. The measuring device is normally called a four point probe and as long as the conductive film is thinner than the distance between the terminals s, it can measure the two dimensional sheet resistance.

3.6.3.3 Resistance Procedure

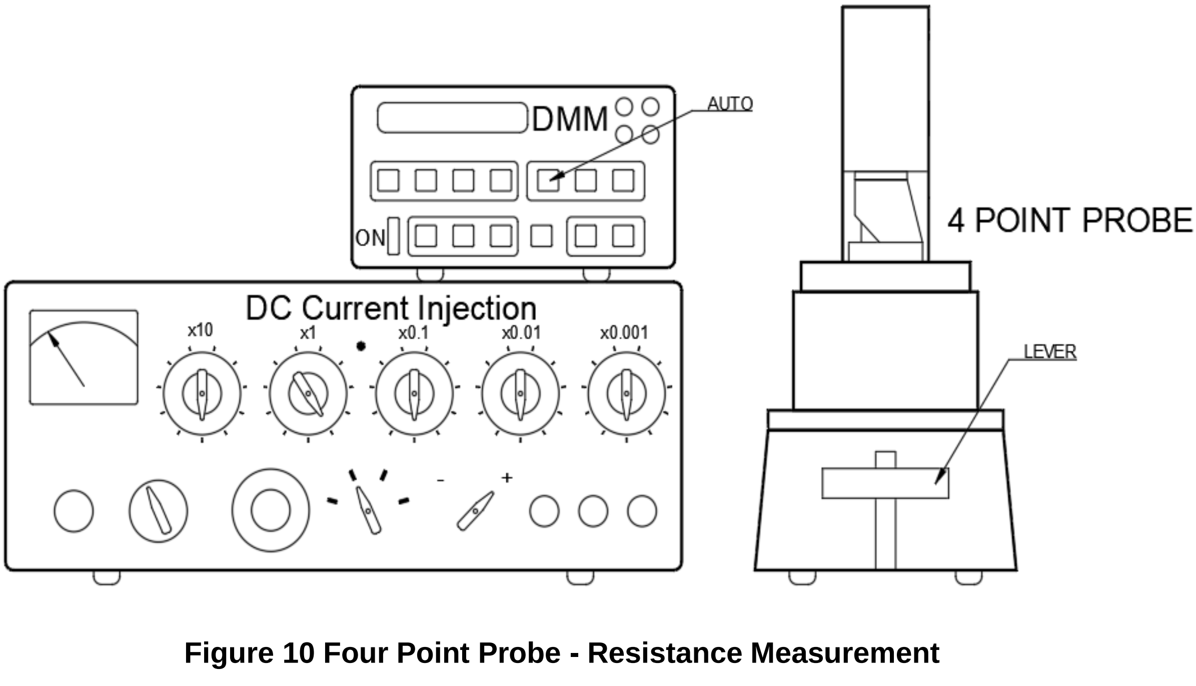


Figure 10 Four Point Probe - Resistance Measurement

Switch equipment on, press “Auto”. Place sample slide under 4-point probe and push lever down to secure. Turn the x1 mA dial to “1” which injects 1 mA into the 4-point probe and note the results shown on display in mV. Repeat between 1 mA and 10 mA noting the mV on each occasion. If the display fluctuates wildly and it's difficult to take a reading, then the sample is probably very high resistance and therefore very little conductance. Try releasing the lever and moving the sample slightly and repeat to try and find a more favourable steady reading. Repeat to obtain at least 3 sets of readings, apply Equation 7 in each case to obtain sheet resistance and take the average of all readings.

3.6.4 Transmission (Spectrophotometry)

Everything absorbs, transmits or reflects light of varying wavelengths. Spectrophotometry measures how much is absorbed or transmitted over specific wavelengths. Basically, a spectrometer measures the number of photons that are transmitted through a sample over a frequency range.

3.6.4.1 Transmission Equipment

Jasio V-670 Spectrometer with software

3.6.4.2 Transmission Procedure

Before any samples can be measured, the system must be run in air to obtain a trace without restriction, the baseline. As it was not possible to cure NW's on PET with the UV lamp, only glass samples were tested. The slides tested were about 15 mm x 60 mm. Once the ambient air test has run, a blank glass test should be made with the same glass slide batch that was used to cure the NW's on. This gives a proper baseline of how much light is transmitted through bare glass first. This can then be compared with tests done on glass slides with varying film thicknesses of NW's.

The wavelength range scanned is between 350 nm to 2500 nm.

3.6.5 XRC using XRD

X-Ray Crystallography (XRC) can be used to determine the atomic and molecular structure of a crystal. The electrons around the crystal cause the x-ray radiation to be scattered in many directions. By measuring the angles and intensities of these detracted beams, it is possible to determine the electron density within the crystal. From these 3D electron densities, the position of the atoms in the crystal can be determined.

3.6.5.1 XRD Equipment

X-ray diffractometer (XRD, model D5005, Siemens)

3.6.5.2 XRD Procedure

The detector analyses angles between 0° to 90° but from experience we know that we only need to analyse between 40° to 80° to obtain better resolution. The signals received by the detector are processed and represented as a 2D diffraction pattern (intensity vs 2θ). The position of these diffraction peaks can be compared to the Joint Committee on Powder Diffraction Standards (JCPDS) data base to determine the crystal structure.

The procedure to prepare a sample on a glass slide is as follows. Prepare the NW's to be measured by mixing in IPA and vortex to obtain a homogeneous mixture. Drop a layer of solution onto the slide. Allow to dry and repeat. The coating needs to be at least 10 µm thick producing a dark layer on the glass. This will use a considerable amount of NW's which can be recovered after XRD tests by scraping off and thoroughly mixing with IPA again in a 10 ml vial.

The speed of the scan is set to 2.4°/min. To determine the crystal structure, compare the X-Ray diffractogram to the Powder Diffraction Files using the software, "DIFFRAC.SUITE EVA".

4 PROCESSES, PROCEDURES AND PLAN

Because there are over 130 separate processes, it was decided to complete a Critical Path Analysis (CPA) early on to both better define these processes and attempt to find the most efficient route through them. Once complete, because of the lack of decision points, it did not make any difference to the route taken but it did enable me to plan my time better as not all the processes demanded all of my time and, with planning, I could perform multiple tasks concurrently.

4.1 Processes

This original list of processes and procedures came from an SOP prepared by Quentin Lonne, the postdoc at Cranfield University that this work follows [27]. For this SOP see Appendix A.

4.1.1 CPA

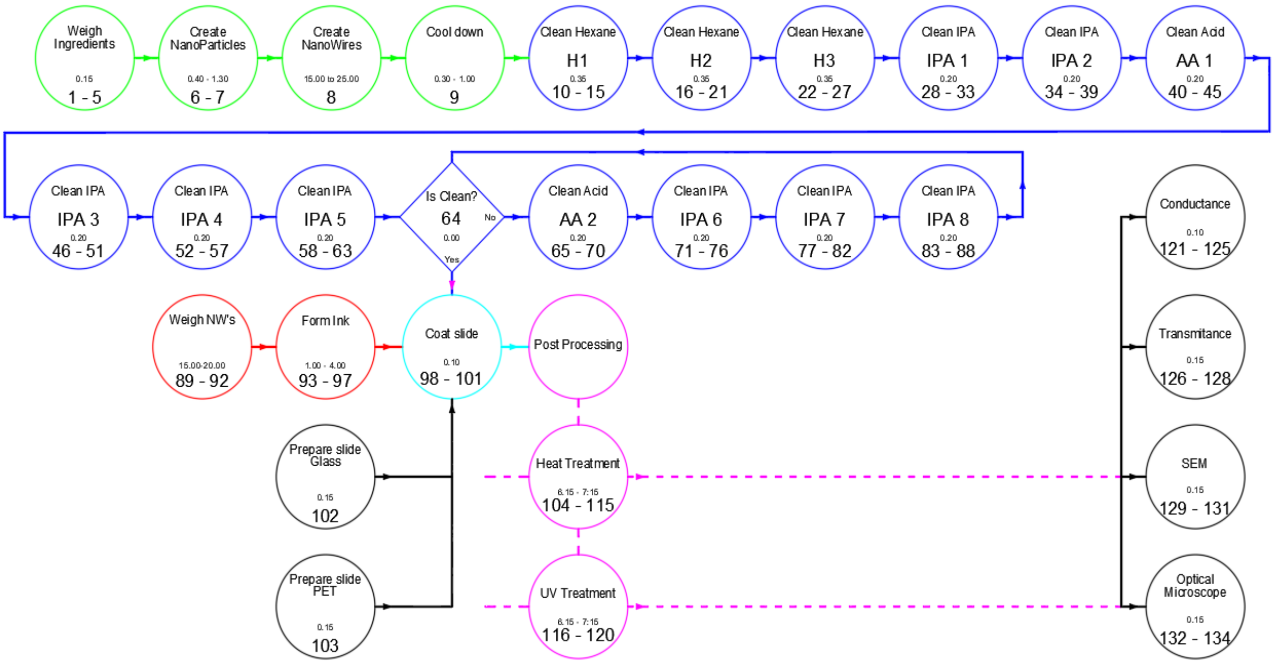


Figure 11 Critical Path Analysis (CPA) Outline

To enable the processes to be seen, an outline has been drawn in Figure 11 that groups similar processes together. An expansion of the first group (1 – 5) is shown below in Figure 12 and the rest are shown in Appendix B.

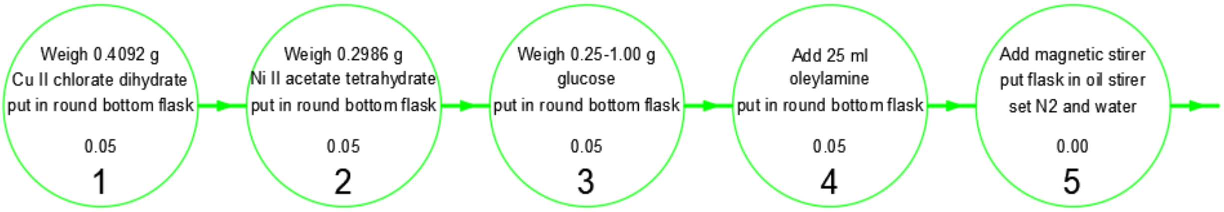


Figure 12 CPA Details Processes 1 to 5

The process number is shown at the bottom of each circle with each process estimation time shown directly above in minutes. A process summary description is shown at the top. The process flow follows the arrows. Where a decision is necessary a diamond shape is used with a single input and with two outcomes following.

The processes have also been colour coded into the relevant groups shown below in Figure 13:

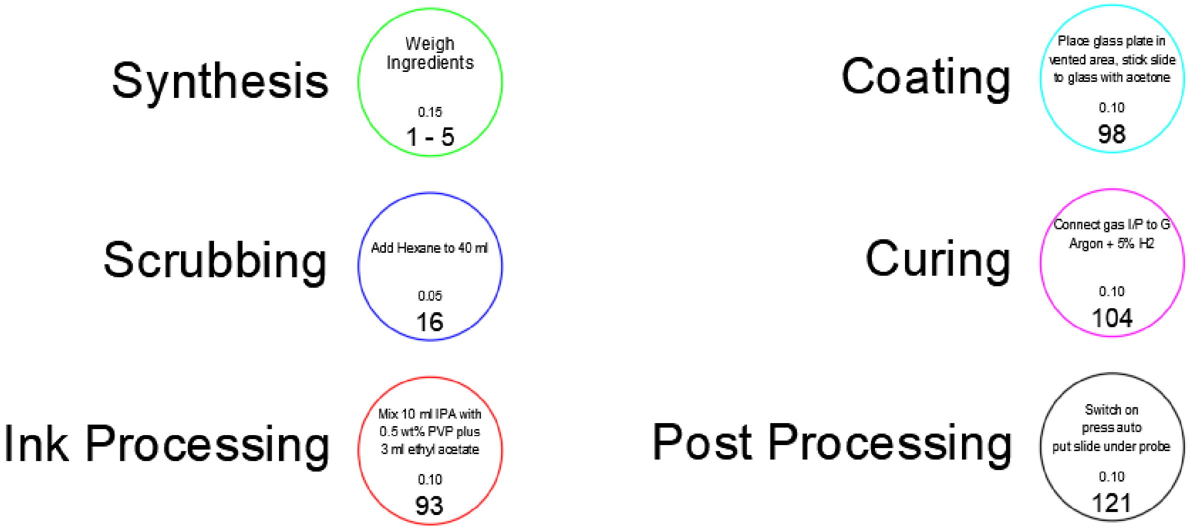


Figure 13 Colour Key for CPA

The first few syntheses, were not completely clean by the end of the scrubbing processes and some had to be cleaned further. Various techniques were found to fix this process. Firstly it was found that if more of the supernatant could be extracted following the centrifuge process, then the solution got cleaner faster. To enable this, the scrubbing bottle must be carried very carefully to the processing area inside the fume hood. Secondly, it also helped when 2 minutes was increased to 3 minutes when manually vortexing the hexane solutions. Finally, increasing the very first centrifuge time from 20 minutes to 25 minutes was found to be effective because the oleylamine solution is very dark making it difficult to see if the NW's have separated properly. Problems were also encountered with NW's clumping together in bundles between the IPA and acetic acid cleaning processes. It was found that if the acetic acid followed the hexane scrubbing, the situation improved. A fourth hexane was used following the acetic acid to prevent bundling. It seems that IPA does not mix so well with acetic acid and causes NW's to clump together into bundles. The final CPA outline is shown in Appendix C and the expansion of these groups in Appendix D.

When the process was first switched off and allowed to cool to 60 °C before the scrubbing process started, often a conglomerated lump was found inside the 50 cl round bottom flask when transferring to the scrubbing bottle. It was found that if the stirrer was started, initially at 800 rpm, when the heat was first turned off, then after 10 minutes it was turned down to 400 rpm, the lump was largely dispersed, and cleaning of the NW's became much easier.

A revised SOP can be found in Appendix E that includes any amendments.

4.2 Plan

As there was limited time and many time consuming processes, it was important to prepare a plan for the allocation of research time. This was prepared in Excel using the information from the CPA. This enabled more efficient use of time, enabling more syntheses to be done and ensuring the research was as comprehensive as possible, given the timeframe.

4.2.1 Synthesis, Scrubbing and Heat Treatment Plans

The most time consuming processes are scrubbing the NW's and to a slightly lesser extent, the NW synthesis. Once the synthesis process has been started, it needs time (15 – 18 hours) to run its course so it was often most efficient to begin synthesis in the afternoon, left to run overnight and stopped in the morning. Once allowed to cool naturally, with the N_2 and water still flowing, the scrubbing process started immediately and took all morning. Therefore, time usually revolved around the scrubbing processes which is the most time demanding but not continuous so other process can be started while centrifuging for 20 minutes for example.

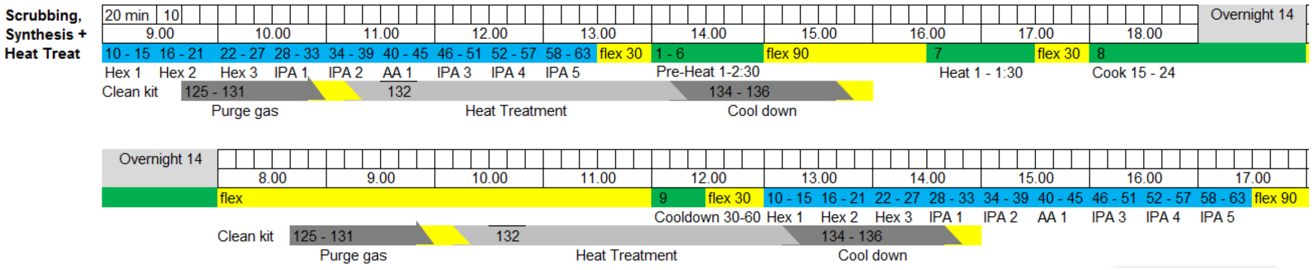


Figure 14 Synthesis Time Plan

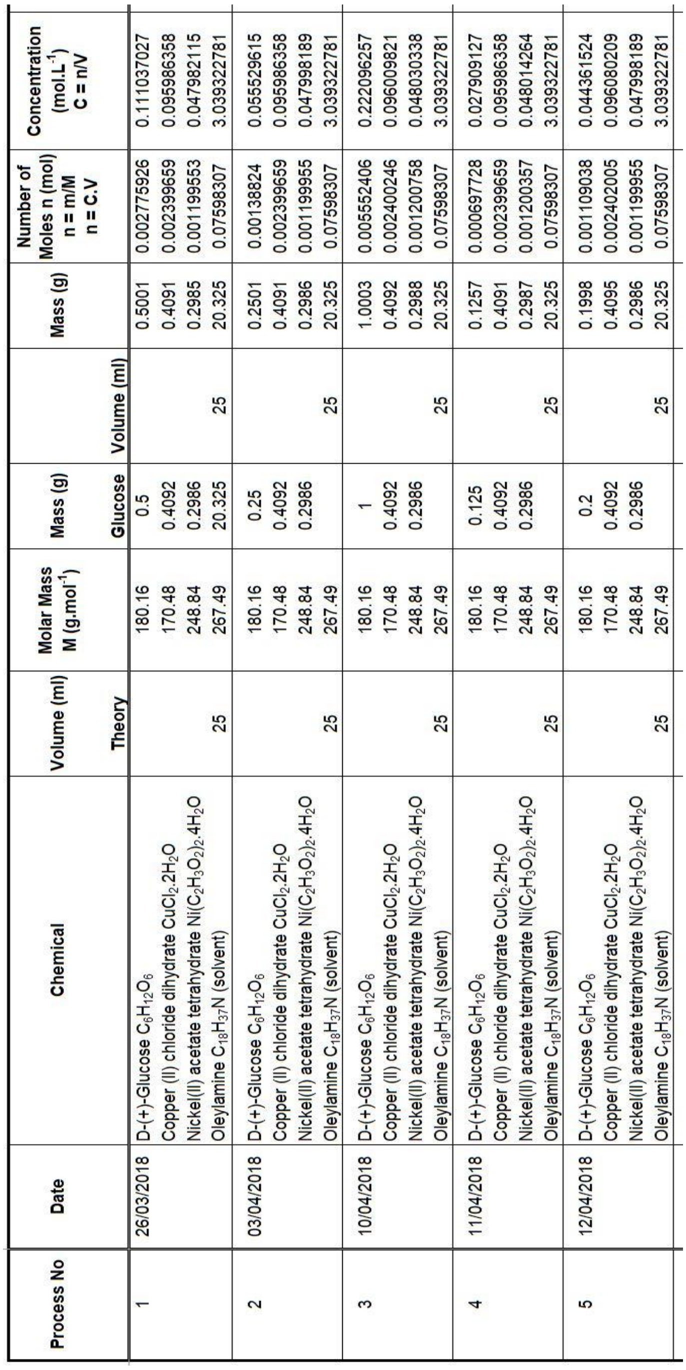
When a synthesis started the previous afternoon (Tuesday, Wednesday & Thursday), scrubbing could start first thing in the morning finishing around lunchtime and another synthesis could begin in the afternoon. The first scrubbing processes use Hexane which requires at least 20-25 minutes centrifuge to separate the NW's from the supernatant. During these periods, it is possible to start a heat treatment to cure the NW's on glass. The main heat treatment process takes 3 hours (6-7 in total) but it's not necessary to be present all the time as long as a notice is left by the equipment stating your name, contact number and time period of the process. The heat treatment requires purging of oxygen and water and also requires time to get up to temperature, so these can be fitted during the centrifuge periods. There are also periods of time (marked yellow) that are flexible, and no harm is done if left for short periods of time to allow processes to be run concurrently. Most of the other processes are independent and can be performed in isolation, so these can be done on a Monday morning and Friday afternoon or any days that a synthesis is not possible for other reasons. Although plenty of running around between buildings was necessary, it was possible to produce 4 syntheses and 5 heat treatments a week at best.

4.3 Data Recording

Where possible, the data was kept together in one place so that any characteristics could be easily compared. Excel is perfect for this purpose because rows and columns can be hidden and printed out from the visible table only. Data can be copied to another tab and charts taken from the visible data while being sorted and preserved. As the spreadsheet is so wide it's not practical to print out in one because it will not be possible to read the data. Most data tables presented in the results will be from this spreadsheet in part.

4.3.1 Example of typical data in spreadsheet

An example, showing the first third of the first five syntheses is shown below: -



Process No	Date	Chemical	Volume (ml)	Molar Mass M (g.mol^{-1})	Mass (g)		Mass (g)	Number of Moles n (mol) n = m/M n = C.V	Concentration (mol.L^{-1}) C = n/V
			Theory		Glucose	Volume (ml)			
1	26/03/2018	D-(+)-Glucose $C_6H_{12}O_6$		180.16	0.5		0.5001	0.002775926	0.111037027
		Copper (II) chloride dihydrate $CuCl_2.2H_2O$		170.48	0.4092		0.4091	0.002399659	0.095986358
		Nickel(II) acetate tetrahydrate $Ni(C_2H_3O_2)_2.4H_2O$		248.84	0.2986		0.2985	0.001199553	0.047982115
		Oleylamine $C_{18}H_{37}N$ (solvent)	25	267.49	20.325	25	20.325	0.07598307	3.039322781
2	03/04/2018	D-(+)-Glucose $C_6H_{12}O_6$		180.16	0.25		0.2501	0.00138824	0.055529615
		Copper (II) chloride dihydrate $CuCl_2.2H_2O$		170.48	0.4092		0.4091	0.002399659	0.095986358
		Nickel(II) acetate tetrahydrate $Ni(C_2H_3O_2)_2.4H_2O$		248.84	0.2986		0.2986	0.001199955	0.047998189
		Oleylamine $C_{18}H_{37}N$ (solvent)	25	267.49		25	20.325	0.07598307	3.039322781
3	10/04/2018	D-(+)-Glucose $C_6H_{12}O_6$		180.16	1		1.0003	0.005552406	0.222096257
		Copper (II) chloride dihydrate $CuCl_2.2H_2O$		170.48	0.4092		0.4092	0.002400246	0.096009821
		Nickel(II) acetate tetrahydrate $Ni(C_2H_3O_2)_2.4H_2O$		248.84	0.2986		0.2988	0.001200758	0.048030338
		Oleylamine $C_{18}H_{37}N$ (solvent)	25	267.49		25	20.325	0.07598307	3.039322781
4	11/04/2018	D-(+)-Glucose $C_6H_{12}O_6$		180.16	0.125		0.1257	0.000697728	0.027909127
		Copper (II) chloride dihydrate $CuCl_2.2H_2O$		170.48	0.4092		0.4091	0.002399659	0.095986358
		Nickel(II) acetate tetrahydrate $Ni(C_2H_3O_2)_2.4H_2O$		248.84	0.2986		0.2987	0.001200357	0.048014264
		Oleylamine $C_{18}H_{37}N$ (solvent)	25	267.49		25	20.325	0.07598307	3.039322781
5	12/04/2018	D-(+)-Glucose $C_6H_{12}O_6$		180.16	0.2		0.1998	0.001109038	0.044361524
		Copper (II) chloride dihydrate $CuCl_2.2H_2O$		170.48	0.4092		0.4095	0.002402005	0.096080209
		Nickel(II) acetate tetrahydrate $Ni(C_2H_3O_2)_2.4H_2O$		248.84	0.2986		0.2986	0.001199955	0.047998189
		Oleylamine $C_{18}H_{37}N$ (solvent)	25	267.49		25	20.325	0.07598307	3.039322781

Table 4 Example of data in Spreadsheet

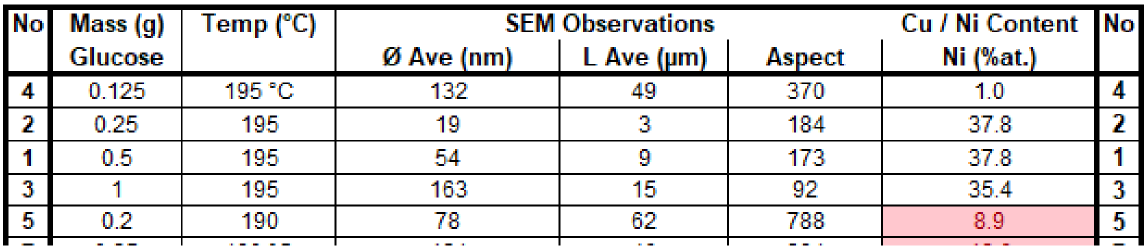
The entire table for the first 5 syntheses is shown in Appendix F tables Table 28, Table 29 and Table 30. Each time a synthesis is done, the ambient temperature and humidity at the start and end of the process is taken. In the first 2 or 3 syntheses, the temperature and humidity are absent as a thermometer was not initially available. Although the ambient conditions do not appear to vary much in this table sample, throughout the project they did. The lab temperature varied between 17.7 - 25.5 °C and the humidity between 33 – 53% during synthesis. The highest recorded ambient lab temperature was 32.5 °C but not during synthesis. Sometimes there was a large variation between starting and ending temperatures and humidity.

5 RESULTS

5.1 Copper-Nickel Nanowire Synthesis

5.1.1 High Temperature – Vary Glucose

A systematic approach was taken, initially keeping the temperature constant at 195 °C while varying the glucose quantity between 0.25 g and 1.00 g. Once analysed it was found that each synthesis produced NW's containing over 35% nickel. Also, the aspect ratio was less than 185. There was also a problem attaining the synthesis temperature of 195 °C. The system seemed to be losing heat at least as quickly as it was input so to hold the temperature above 190 °C was very difficult. As one of the aims of this research was to synthesise NW's of between 5 – 20% nickel, it was run again with reduced glucose (0.2 and 0.125 g). Also, a lid to cover the oil bath was made from many layers of shiny aluminium foil so as to reflect some of the lost heat back into the system rather than it being lost. This was very successful, and it was then possible to maintain the high temperature more consistently.



No	Mass (g) Glucose	Temp (°C)	SEM Observations			Cu / Ni Content	No
			Ø Ave (nm)	L Ave (µm)	Aspect	Ni (%at.)	
4	0.125	195 °C	132	49	370	1.0	4
2	0.25	195	19	3	184	37.8	2
1	0.5	195	54	9	173	37.8	1
3	1	195	163	15	92	35.4	3
5	0.2	190	78	62	788	8.9	5

Table 5 Synthesis 190-195 °C Vary Glucose

This table (Table 5) is made from Table 4 with column and rows hidden leaving only items of interest, then sorted by temperature and glucose. The aspect ratio highlighted in red uses conditional formatting to highlight values above 400 (first aim). Synthesis No 5 (0.2 g glucose) was the first synthesis using the foil lid to maintain better control of temperature. The temperature was therefore reduced to 190 °C to be closer to the real synthesis temperature of the first four.

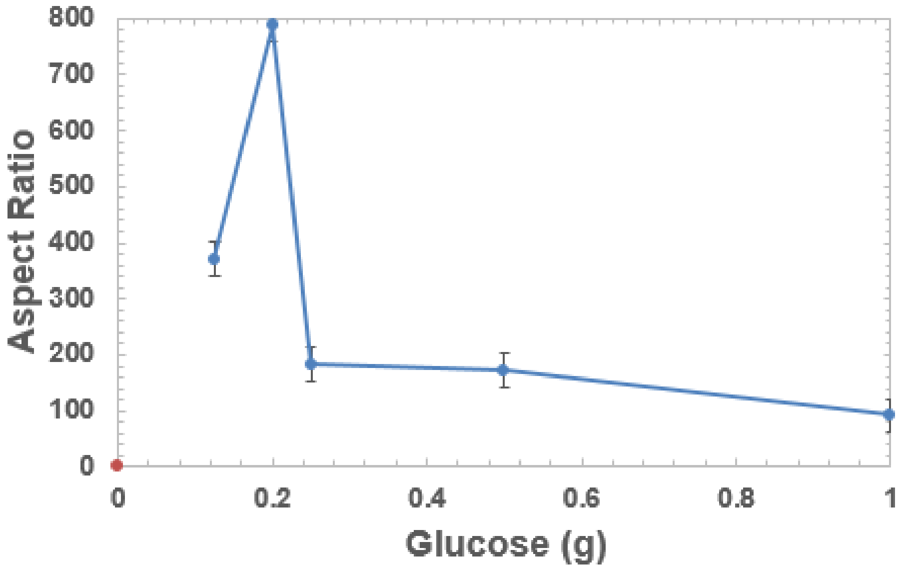


Figure 15 Syntheses 190-195 °C Glucose vs Aspect Ratio

Figure 15 above plots the Glucose content against the Aspect Ratio. The glucose error measurements are considered to be insignificant compared to the aspect ratio calculations. The glucose was weighed accurately to 3 decimal places whereas the aspect ratio is an average measurement of NW diameters and lengths taken from SEM micrographs. It is expected that the NW diameters will be more accurate than the lengths because the magnification is greater (typ. 10000-50000 times). To capture NW lengths the magnification is typ. 1000-2500 times magnification which can be difficult to measure curved wires when they overlap considerably with each other. Therefore error bars have been included for ±30 of the aspect ratio. Nickel content is also considered a quite accurate EDS measurement (±1%) so error bars are not included.

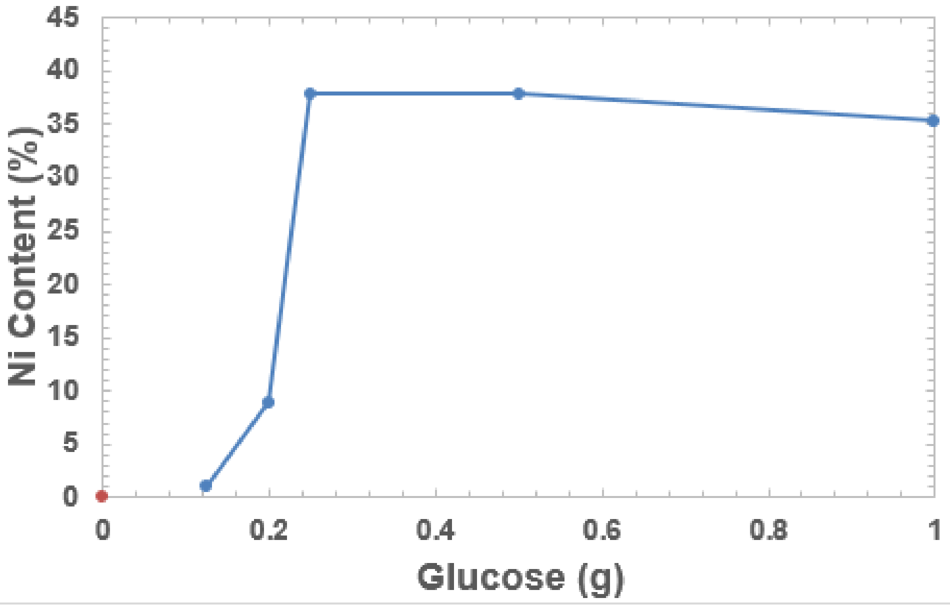


Figure 16 Syntheses 190-195 °C Glucose vs Ni Content

Figure 16 above plots the Glucose content against the Nickel content.

5.1.2 Lower Temperature – Vary Glucose

The synthesis temperature was lowered until the process appeared to stop working which was at around 160 °C. It was later found that others had been using the equipment and glassware and that the initial setup was not as it should have been which affected the results. It was therefore decided to clean glassware both after use and prior to use in case it had been contaminated and not cleaned properly. Care was taken to set up the equipment prior to each synthesis. It was found that with these extra precautions, the synthesis appeared to work below the 160 °C level right down to 115 °C. However, once analysed, it was found that although the aspect ratio was very good down to 125 °C (over 500), no nickel was included into the nanowires. The best synthesis obtained in the time available was at 160 °C although it was felt that 155 °C might be possible with the addition of more glucose (1.25 g) to increase the Ni content.

Temp (°C)	No	Glucose (g)	Aspect Ratio
195 °C	4	0.125	370
195	2	0.25	184
195	1	0.5	173
195	3	1	92
180 °C	7	0.25	381
180	16	0.5	507
180	38	0.5	260
180	8	0.75	158
175 °C	25	0.25	481
175	24	0.5	764
175	26	0.6	417
175	23	0.75	367
170 °C	9	0.25	622
170	15	0.5	242
170	10	0.75	535
170	11	1.25	329
165 °C	29	0.5	539
165	40	0.6	750
165	28	0.75	456
165	27	1	429
160 °C	12	0.25	522
160	14	0.5	406
160	13	0.75	536
160	39	1	522
160	19	1.25	196

Table 6 Lower Temperature Aspect Ratio Data

Table 6 above shows the data used for the data points in Figure 17 below.

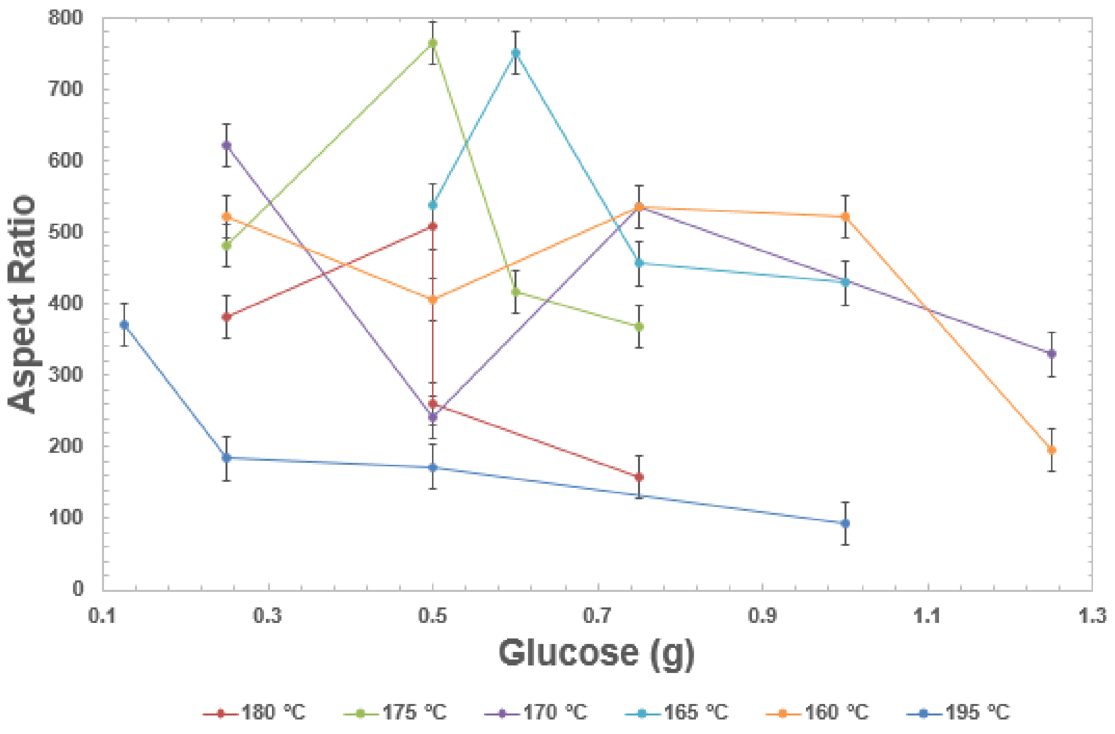
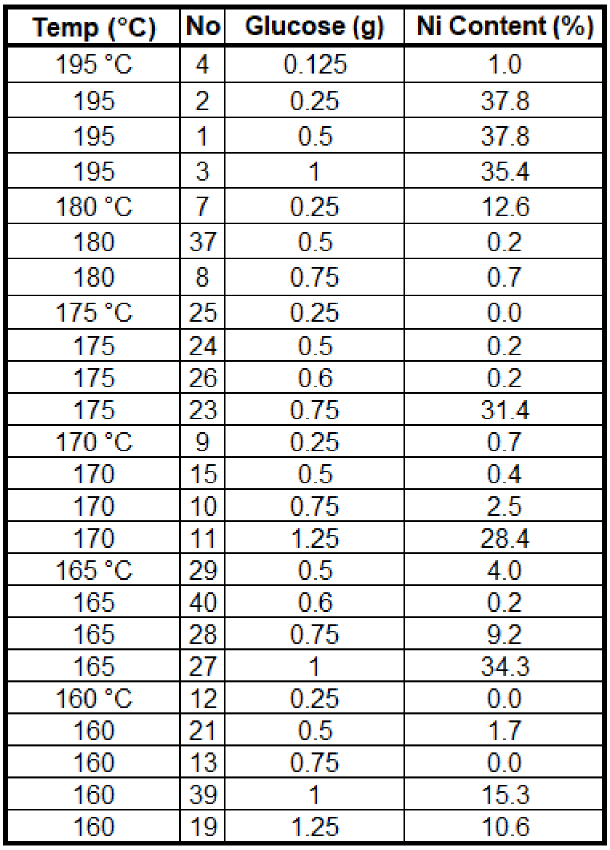


Figure 17 Temperature Varied - Glucose vs Aspect Ratio

Straight lines are included between the data points to show associations between the points. Without the lines, even if the point style is varied between data sets, it is almost impossible to understand clearly.



Temp (°C)	No	Glucose (g)	Ni Content (%)
195 °C	4	0.125	1.0
195	2	0.25	37.8
195	1	0.5	37.8
195	3	1	35.4
180 °C	7	0.25	12.6
180	37	0.5	0.2
180	8	0.75	0.7
175 °C	25	0.25	0.0
175	24	0.5	0.2
175	26	0.6	0.2
175	23	0.75	31.4
170 °C	9	0.25	0.7
170	15	0.5	0.4
170	10	0.75	2.5
170	11	1.25	28.4
165 °C	29	0.5	4.0
165	40	0.6	0.2
165	28	0.75	9.2
165	27	1	34.3
160 °C	12	0.25	0.0
160	21	0.5	1.7
160	13	0.75	0.0
160	39	1	15.3
160	19	1.25	10.6

Table 7 Lower Temperature Ni Content Data

Table 7 above shows the data used to produce Figure 18 below.

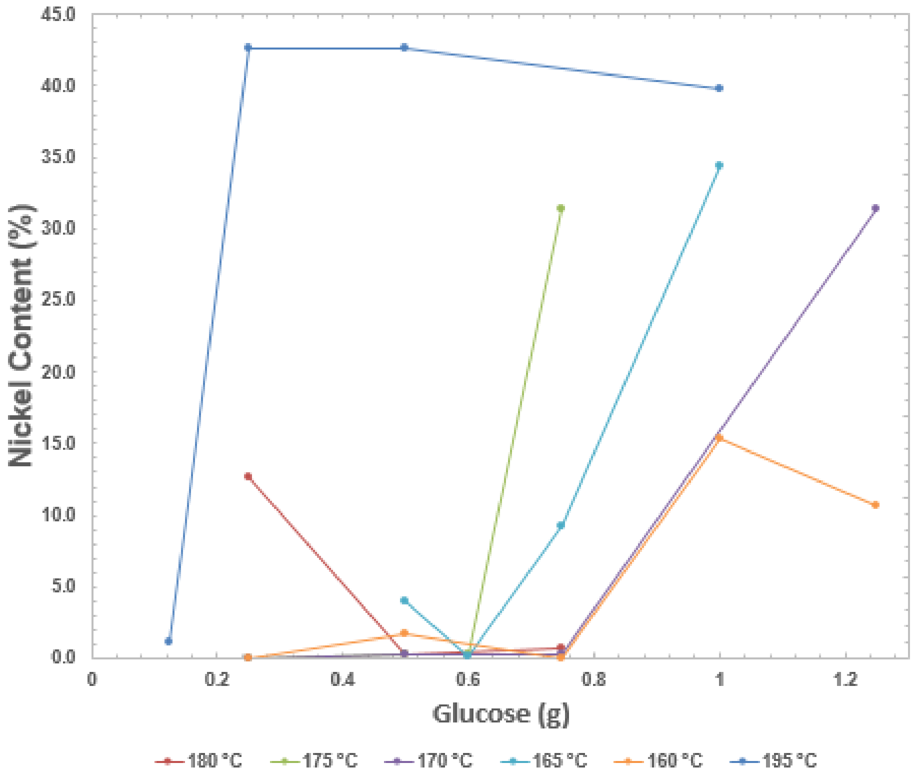


Figure 18 Temperature Varied - Glucose vs Nickel Content

5.1.3 First Aim – Increase Aspect Ratio > 400

The first aim (1) is to increase the aspect ratio to above 400. To investigate the aspect ratio at different temperatures further, which is the main aim it is necessary to keep everything constant except temperature. There are more syntheses when the glucose content is 0.75 g than any other, going almost across the entire range, except for 195 °C. The data for 0.75 g glucose is shown below in Table 8; -

No	Glucose (g)	Temp (°C)	Aspect	Ni (%at.)
8	0.75	180	158.46	0.68
23	0.75	175	367.30	31.40
10	0.75	170	534.81	2.50
28	0.75	165	456.07	9.17
13	0.75	160	536.13	0.00
30	0.75	155	737.59	0.66
32	0.75	145	921.73	0.00
34	0.75	135	494.70	0.15
35	0.75	125	514.34	0.00
36	0.75	115	128.01	0.02

Table 8 Glucose Constant at 0.75 g - Vary Temperature

The cells to the right of Table 8 are highlighted red to show Ni content within the second aim range (5-20%). The cells highlighted red (0.75) in glucose column, mean that the Ni compound content weight was 0.3285 g rather than 0.2986 g.

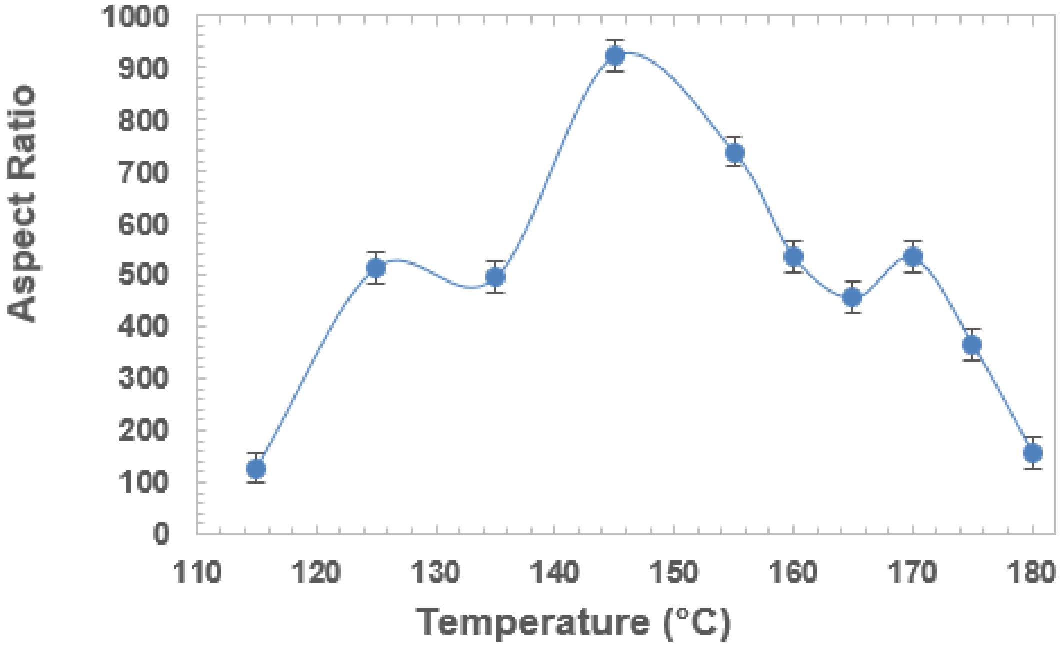
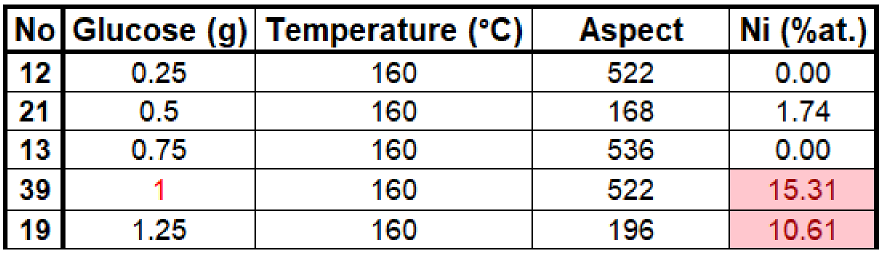


Figure 19 Aspect Ratio vs Temperature - Glucose 0.75 g

This produces an interesting curve shown in Figure 19 which is reasonably symmetrical. Although there are a couple of bumps in it, the curve appears to have an optimum aspect ratio of a little over 900 which occurs somewhere between 140 – 150 °C when the glucose is set to 0.75 g. However, the nickel content is in the right proportions (5-20%) between 165-170 °C and so does not coincide with the peak aspect ratio.

5.1.4 Second Aim – Optimise Nickel Content

The second aim (2) was to control the Ni content between 5-20%. From the syntheses results above in section, 5.1.3 the optimum aspect ratio is between 140–150 °C but no glucose is present at these temperatures. To keep the best aspect ratio possible but still fulfil the second aim, the lowest temperature should be chosen that it's still possible to make nanowires with a nickel content between 5-20%. This temperature is 160 °C.



No	Glucose (g)	Temperature (°C)	Aspect	Ni (%at.)
12	0.25	160	522	0.00
21	0.5	160	168	1.74
13	0.75	160	536	0.00
39	1	160	522	15.31
19	1.25	160	196	10.61

Table 9 Temperature 160 °C - Vary Glucose

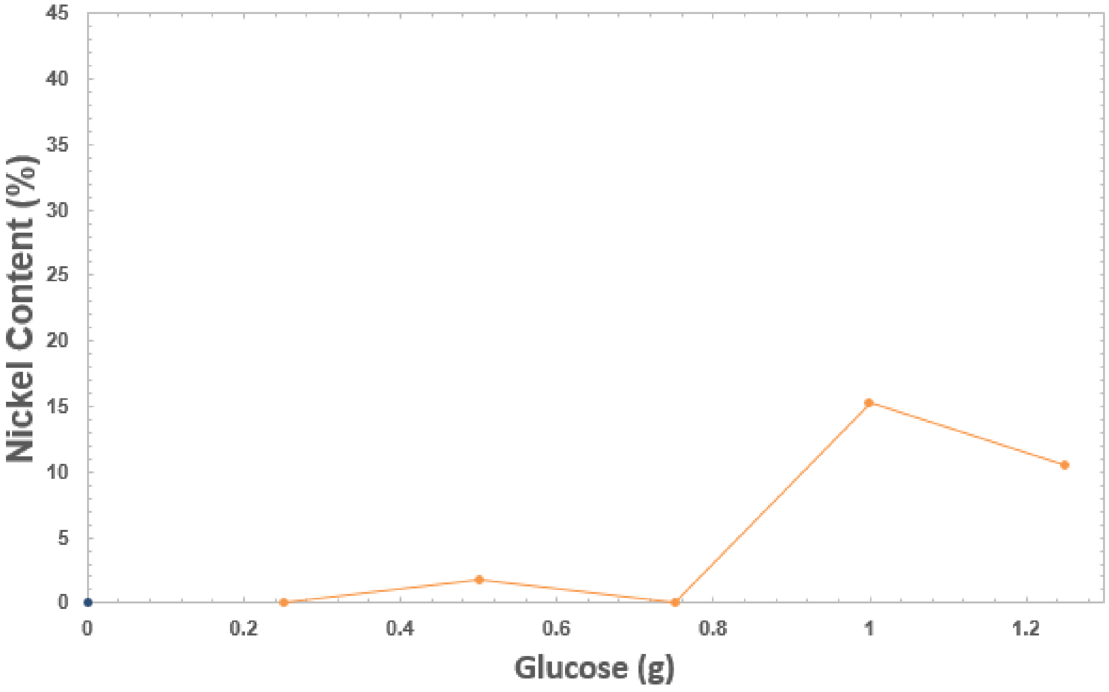


Figure 20 Glucose vs Nickel Content - 160 °C

Figure 20 is Figure 18 with other temperatures removed except for 160 °C. The nickel content within the ideal range is found with glucose between about 0.9 – 1.25 g. From Table 9 it can be seen that two syntheses were done within this range, syntheses 19 and 39. Synthesis 19 has the better nickel content but the aspect ratio is less than 200 so synthesis 39 should be used to make the ink used for the optoelectronic tests. Synthesis 39 was made at 160 °C with 1 g glucose.

5.2 Curing

Two curing methods were attempted in this research, heat curing and UV exposure curing.

5.2.1 Heat Curing

The heat curing procedures and equipment is described in section 3.5.1 and uses a tubular oven set to 350 °C which is not suitable for R2R methods as the temperature is too high. The very first synthesis was made into ink, spread on a glass slides using all three Mayer rods, #12, #8 and #4 then heat treated to demonstrate the procedure and allow optoelectronic testing of the cured slides.

All attempts of heat curing samples worked, except when two samples were tried together. The following inks were all cured using heat treatment.

Synthesis 39	40 mg/ml	#12
Synthesis 39	30 mg/ml	#12
Synthesis 39	20 mg/ml	#12
Synthesis 39	10 mg/ml	#12
Synthesis 39	40 mg/ml	#8
Synthesis 39	40 mg/ml	#4
Synthesis 39	10 mg/ml	#12
Synthesis 28	40 mg/ml	#12
Synthesis 28	20 mg/ml	#12
Synthesis 28	40 mg/ml	#8

5.2.2 UV Curing

The UV Curing procedures and equipment is described in section 3.5.2 and uses a UV exposure box.

Great effort was made to cure NW's on PET using UV exposure because there are so many advantages over heat treatment. This method is known to have worked because Lonne,Q [34] conducted UV curing of copper NW's at Cranfield University in 2016-2017 using the exact same UV light box. The two main advantages are, it is quick – typically a few minutes exposure opposed to more than 6 hours for heat treatment and it is low temperature, so it can be used for flexible R2R technology.

Curing was initially tried on sample 1 on PET for samples made using the #4, #8 and #12 Mayer rods without success, even though exposure times up to 40 minutes were tried. It was tried again using samples 2, 3, 4 and 5 with Mayer rod #12 so the NW layer was thickest, also without success.

One possibility for it not working was because the lightbox was very old and the electrodes that strike the arc, erode slowly and become ineffective, first in the UV, later in the visible. A replacement bulb was purchased and fitted at considerable cost. It was then tried using sample 28 because it has 9% nickel content and an aspect ratio of 456, also without success.

It was proposed that maybe it only works with copper NW's and not CuNi for some reason. The final inks tested were made using inks 31 and 32 which both have an aspect ratio of over 920 and zero nickel content. Wide samples were prepared with each ink and exposed for 4 minutes each without success. Two thirds of the samples were cut off and dipped in acetic acid for 10 minutes and allowed to air dry. The samples were cut in half, exposing one half of each for 4 more minutes UV then testing all four samples for conductivity without success.

This meant that all samples used for optoelectronic testing had to be prepared using heat treatment. Only one curing can be performed per day as the process takes over 6 hours. Two samples were attempted to be cured simultaneously without success which means that only one sample can be cured per day.

5.2.2.1 UV Curing Compare

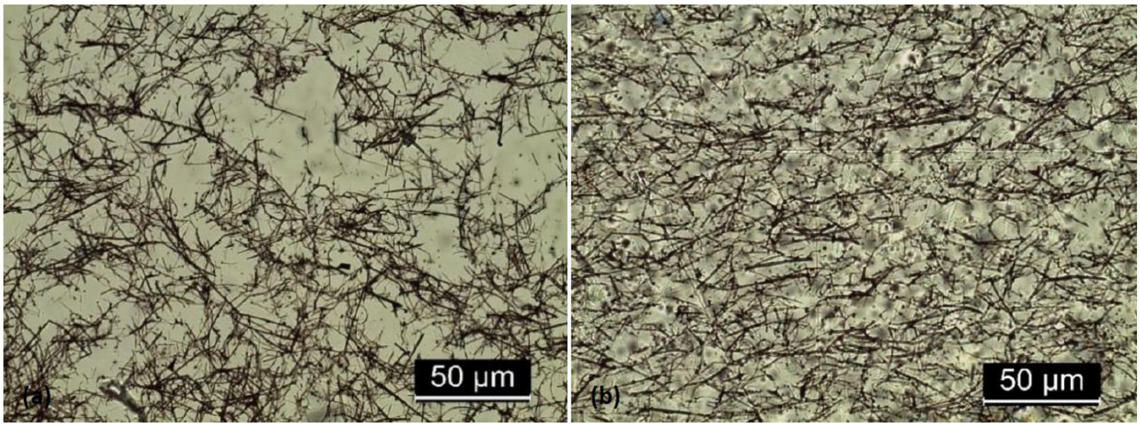


Figure 21 OM Micrographs of HT on Glass vs UV on PET for Synthesis 4

Figure 21 shows micrographs using the optical microscope for synthesis 4. Both had been spread using Mayer rod #12 and then cured. The LH image is heat treated glass and the RH image UV cured on PET (without success). The glass sample was conductive, but the PET sample was non-conductive. Synthesis 4 was synthesised at 190 °C, has an aspect ratio of 370 and only 1% nickel content. The percolation on the PET looks at least as good as on the glass.

5.3 Optoelectronic Testing

Optoelectronic testing consists of two basic parts, conductance testing and transmission testing using various inks.

5.3.1 Inks

Inks are prepared using equipment and procedures in section 3.3. The ink chosen from all 40 synthesised for the optoelectronic testing was synthesis 39. Two more inks were chosen for conductive testing for comparison, syntheses 28 and 29. Synthesis 39 should be the best overall for nickel content of 15% and aspect ratio of 522.

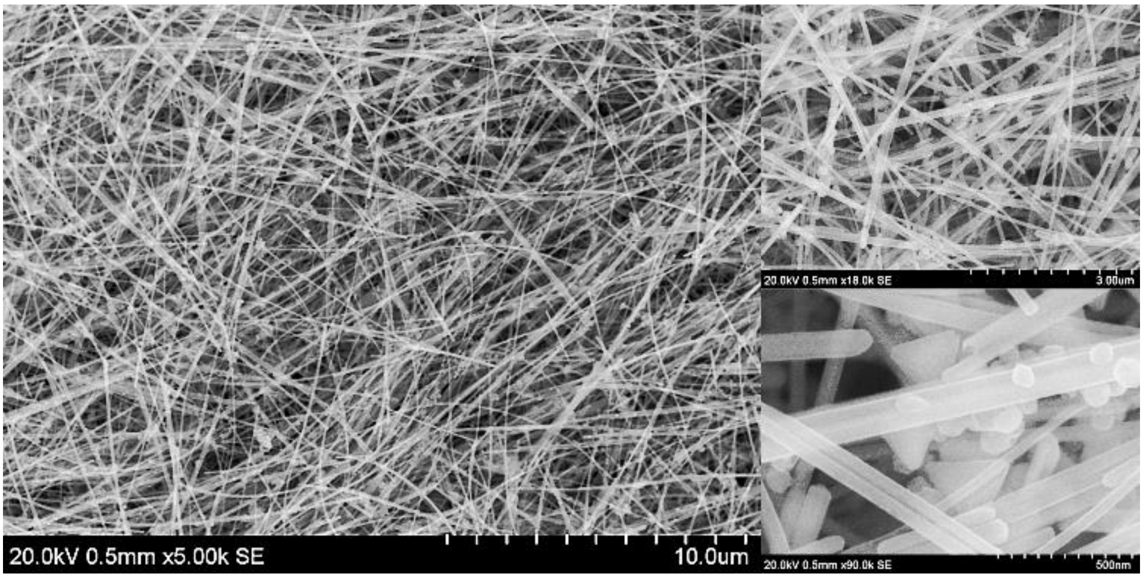


Figure 22 Synthesis 39 Micrograph

Syntheses 28 and 29 were chosen as they have nickel contents of 9% and 4% respectively. They also have good aspect ratios of 456 and 538 respectively. Inks are initially prepared at a concentration of 40 mg/ml, so these were used for initial tests using the #12 Mayer rod. Subsequent tests were done by reducing the concentrations.

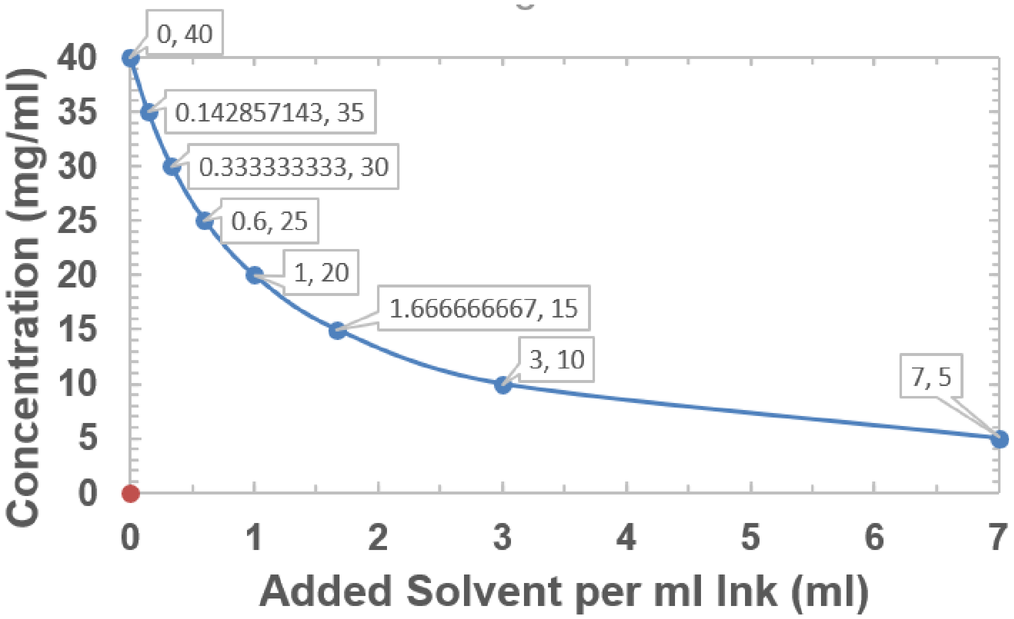


Figure 23 Ink Dilutions from 40 mg/ml Concentration Ink

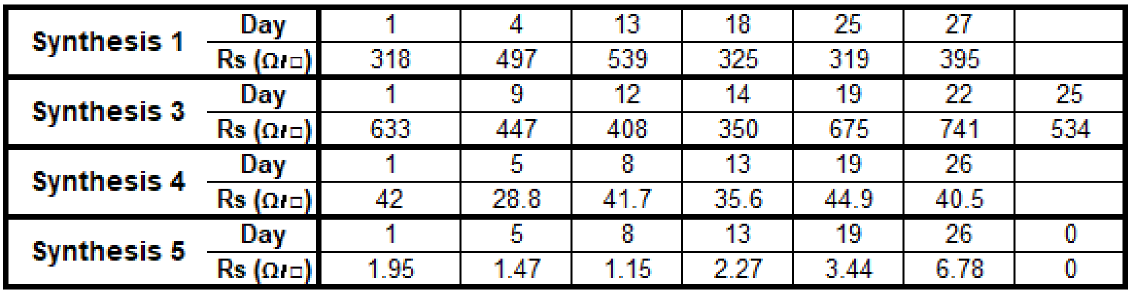
Figure 23 shows how much solvent (virgin ink) to add to each ml of 40 mg/ml initially made ink to obtain the desired concentration of ink. The callout boxes refer to [first number – added solvent (ml), second number – desired concentration (mg/ml)]. For example, to obtain an ink of concentration 10 mg/ml, add 3 ml of solvent to 1 ml of 40 mg/ml ink.

Synthesis 39 inks were made for 40 mg/ml, 30 mg/ml, 20 mg/ml and 10 mg/ml. These were cured using the #12 Mayer rod initially and subsequently using the #4 and #8 Mayer rods. Syntheses inks 28 and 29 with the 40 mg/ml were diluted to 20 mg/ml also for comparison tests.

5.3.2 Resistance Testing

For resistance testing equipment and procedure see 3.6.3. Resistive testing using the four-point probe on glass was carried out.

5.3.2.1 Syntheses 1, 3-5



Synthesis 1	**Day**	1	4	13	18	25	27	
	Rs (Ω/□)	318	497	539	325	319	395	
Synthesis 3	**Day**	1	9	12	14	19	22	25
	Rs (Ω/□)	633	447	408	350	675	741	534
Synthesis 4	**Day**	1	5	8	13	19	26	
	Rs (Ω/□)	42	28.8	41.7	35.6	44.9	40.5	
Synthesis 5	**Day**	1	5	8	13	19	26	0
	Rs (Ω/□)	1.95	1.47	1.15	2.27	3.44	6.78	0

Table 10 Resistance 1, 3, 4 & 5 over Time Data

Table 10 shows initial conductance tests made on first few samples over time to show oxidation processes. Synthesis 1 ink concentration was 40 mg/ml whereas syntheses 3, 4 and 5 were 25 mg/ml. This data is used to plot Figure 24 below: -

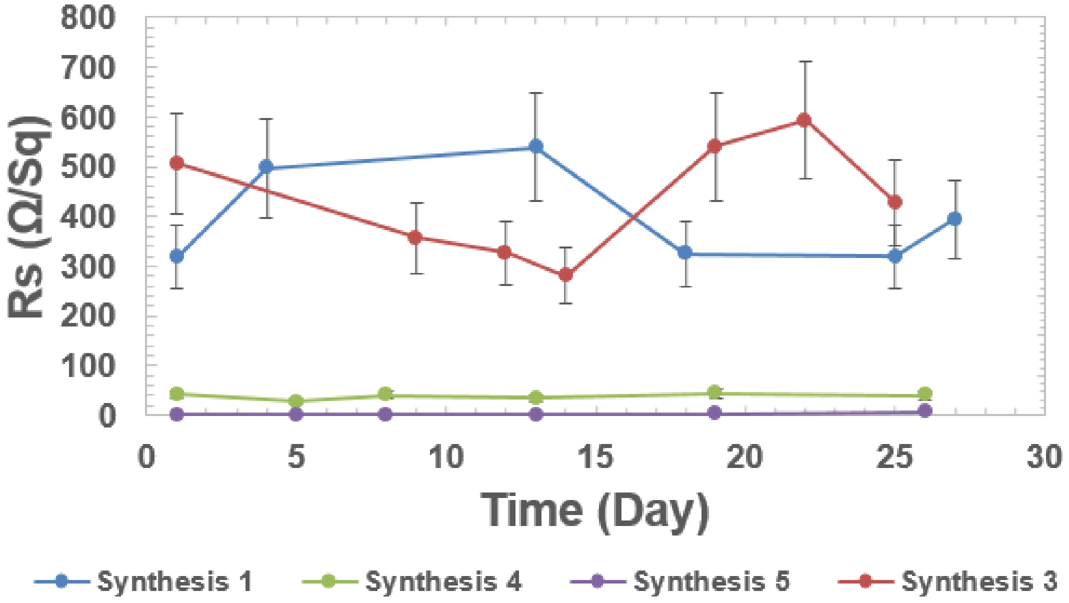


Figure 24 Resistance 1, 3, 4 & 5 over Time

Although the resistance measurements themselves are considered reasonably accurate (1%), the variation in the coating itself varies considerably. According to exactly where the 4 point probe was placed, the reading range changed considerably. For this reason, at least 3 measurements were taken for each point and averaged but also an additional ±20% error has been included to the charts. These samples were initially kept in air during the first tests and then in a 50 °C oven during all subsequent tests.

Other inks prepared for resistive testing are 28, 29 and 39.

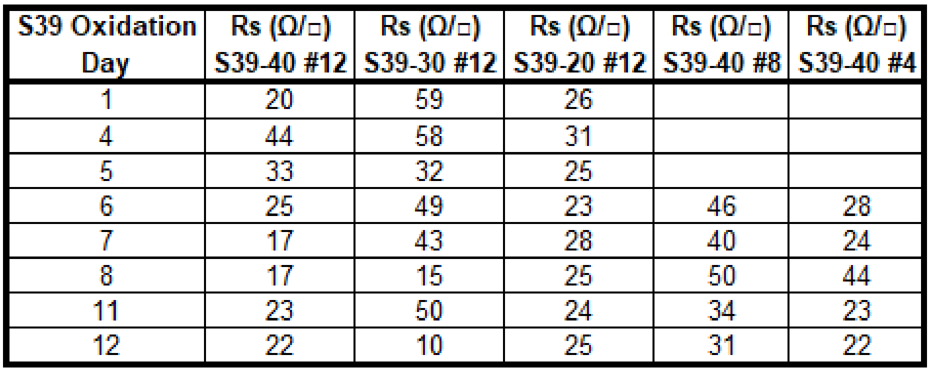
5.3.2.2 Synthesis 39 Resistance

S39 #12 Concentration (mg/ml)	S39 test 1 Rs (Ω/□)	S39 test 2 Rs (Ω/□)	S39 test 3 Rs (Ω/□)	Average Rs (Ω/□)
40	20	25	15	20
30	102	44	30	59
20	30	23	26	26
10	-	-	-	-

Table 11 S39 Resistance Data - Vary Concentration Example

Table 11 is an example of the daily summary of resistance measurements taken for S39 #12 at various concentrations. Each one of the numbers in tests 1-3 are themselves averages of measurements taken between 1 and 10 mA.

The 10 mg/ml ink concentration did not have good percolation and therefore would have been non-conductive so was not cured.



S39 Oxidation Day	Rs (Ω/□) S39-40 #12	Rs (Ω/□) S39-30 #12	Rs (Ω/□) S39-20 #12	Rs (Ω/□) S39-40 #8	Rs (Ω/□) S39-40 #4
1	20	59	26		
4	44	58	31		
5	33	32	25		
6	25	49	23	46	28
7	17	43	28	40	24
8	17	15	25	50	44
11	23	50	24	34	23
12	22	10	25	31	22

Table 12 S39 Data - Resistance Deterioration

Table 12 is a record of S39 resistance over time. Day has the averages recorded on Day 1 from Table 11. S39-40 #8 and S39-40 #4 were not started until a little later after they had been cured.

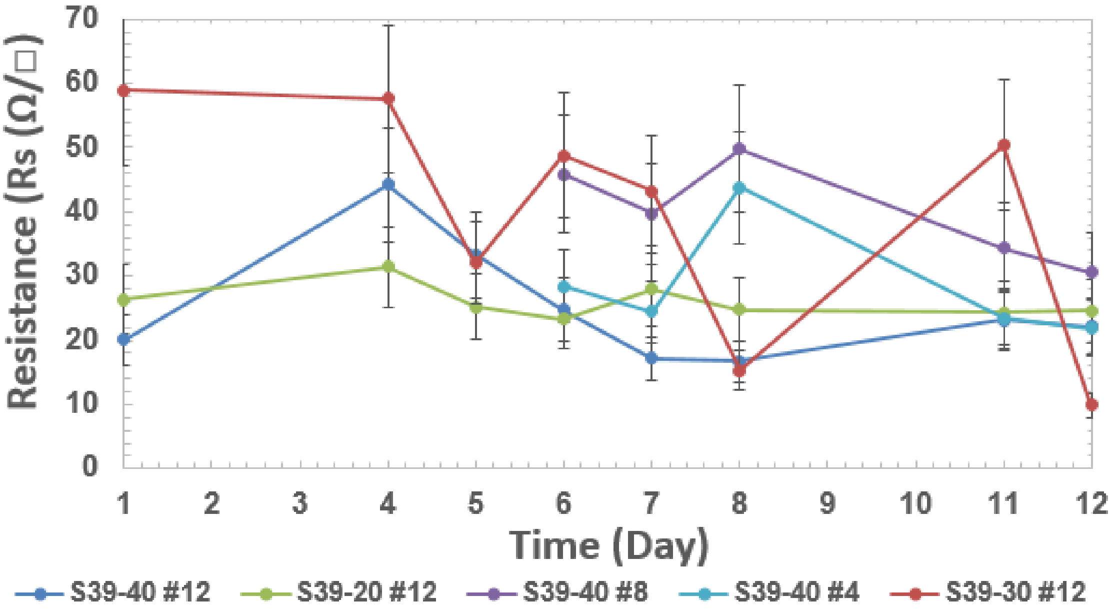
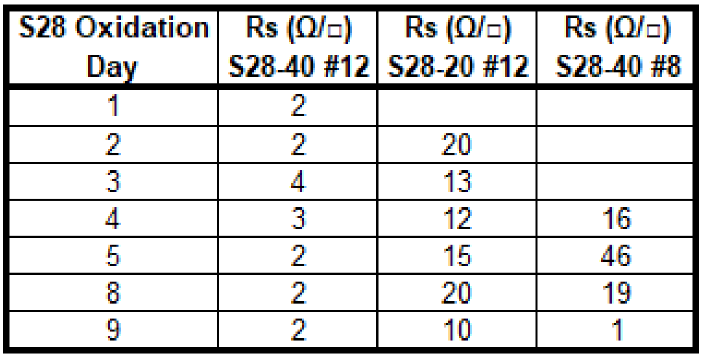


Figure 25 S39 Resistance Deterioration

Figure 25 is plotted from the data in Table 12.

5.3.2.3 Synthesis 28 Resistance



S28 Oxidation Day	Rs (Ω/□) S28-40 #12	Rs (Ω/□) S28-20 #12	Rs (Ω/□) S28-40 #8
1	2		
2	2	20	
3	4	13	
4	3	12	16
5	2	15	46
8	2	20	19
9	2	10	1

Table 13 S28 Data - Resistance Deterioration

Table 13 is a record of S28 resistance over time.

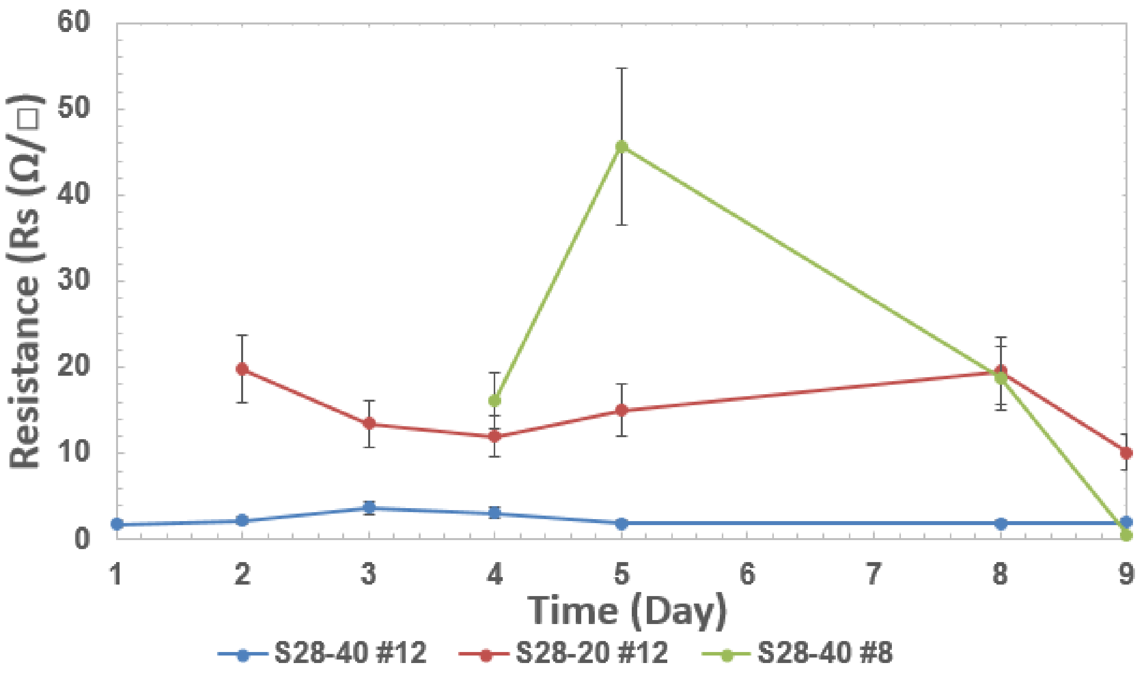


Figure 26 S28 Resistance Deterioration

Figure 26 is plotted from the data in Table 13.

5.3.3 Transmission Testing

For transmission equipment and procedure see 3.6.4.

5.3.3.1 Synthesis 1 Transmissivity

The very first synthesis 1 was cured using the tubular oven. The ink concentration used was 40 mg/ml and spread using the #4, #8 and #12 Mayer rods on glass slides.

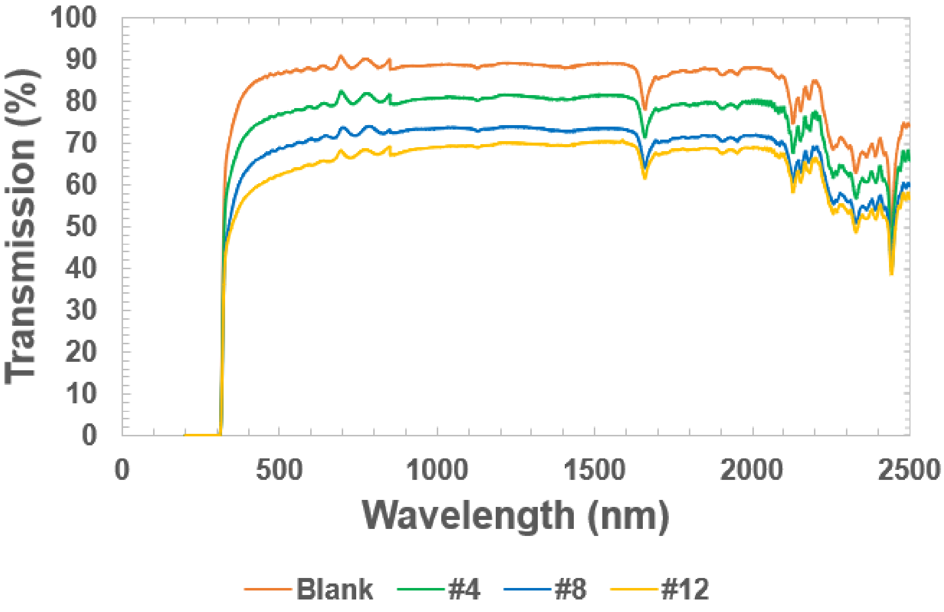


Figure 27 Synthesis 1 on Glass Transmission

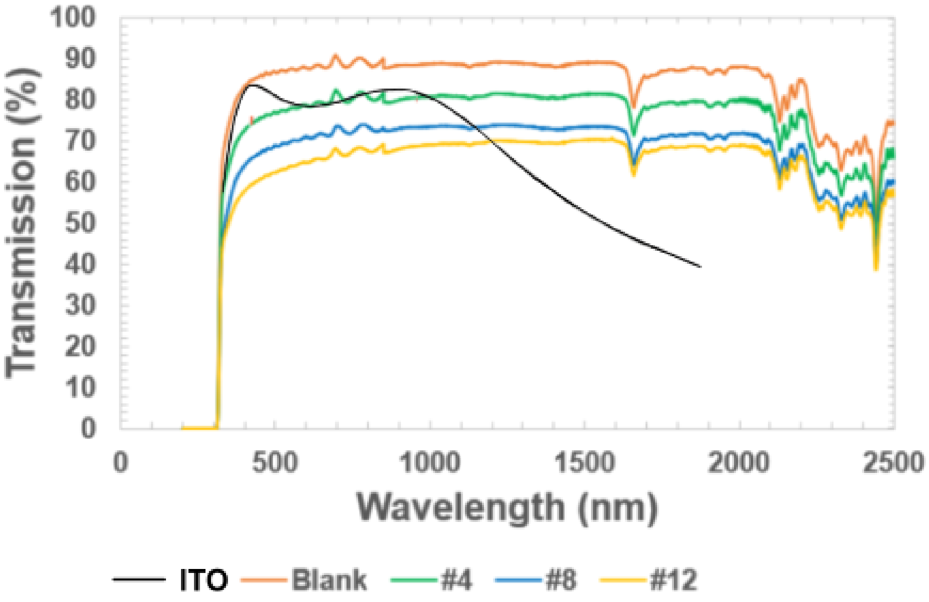


Figure 28 Synthesis 1 on Glass Transmission with ITO

Figure 28 above is the same as Figure 27 but includes an overlay of the transmission for ITO which is the reference (black curve). ITO transmission normally peaks between 350-750 nm at between 90-96% of the transmission of the medium the coating is placed on. Therefore, the ITO curve (black) curve shown in Figure 28 has been adjusted so that it is always below the plain glass curve (red).

5.3.3.2 Synthesis 39 Transmissivity

Sample 39 was chosen as the main ink to carry forward for conductivity and transmissivity tests along with syntheses 28 and 29 for comparison.

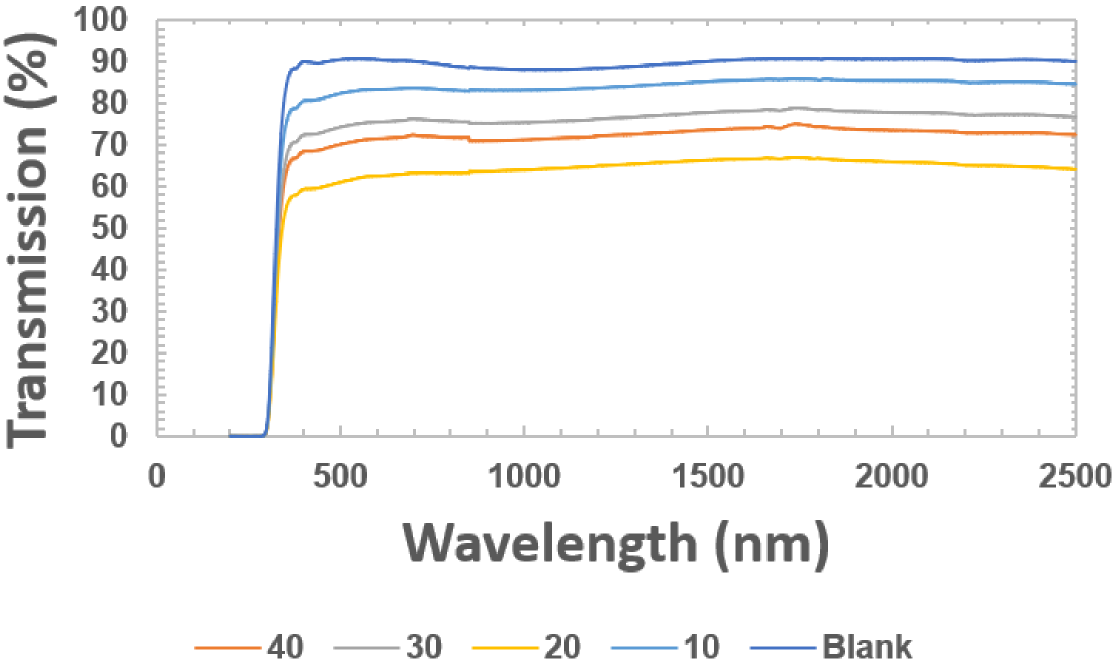


Figure 29 S39 Wavelength vs Transmission – Vary Concentration

The curves in Figure 29, at first glance looks very good. On closer inspection, all is not what it seems. The least transmissive ink is the yellow, 20 mg/ml ink but it would be expected to be the 40 mg/ml ink, followed by the 30 mg/ml ink etc. As this was not the case, a second reading of each was carried out and the average transmission taken and plotted against Wavelength below; -

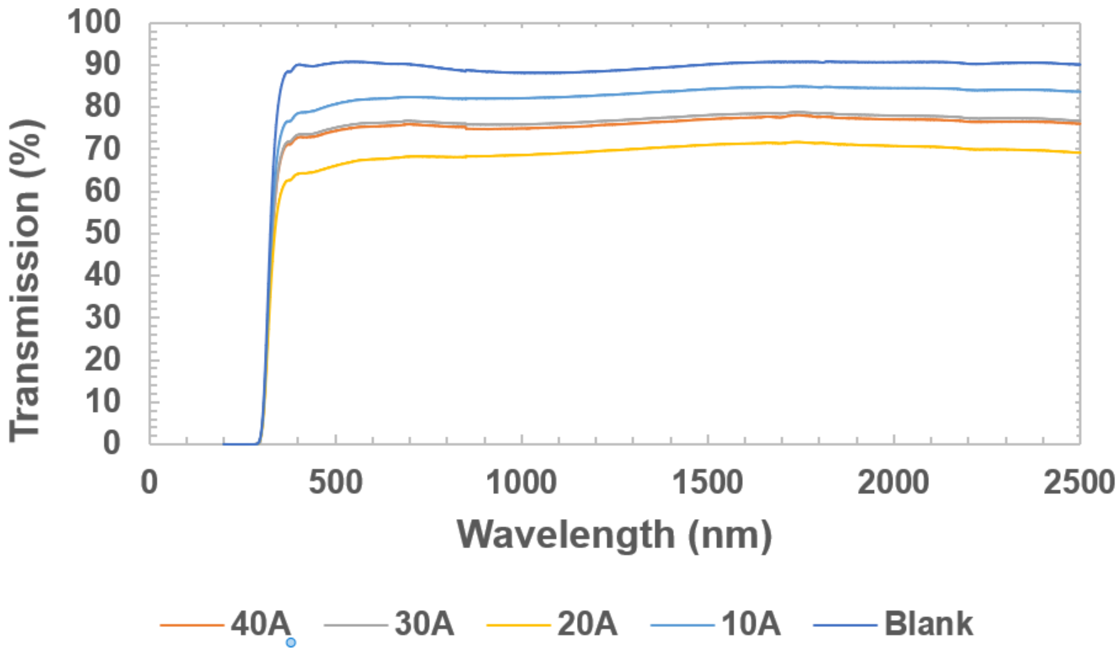


Figure 30 S39 Wavelength vs Transmission – Vary Average Concentration

Here, the yellow 20 mg/ml is still the least transmissive and the 30 and 40 mg/ml inks are about the same as each other while the 10 mg/ml sample the most transmissive.

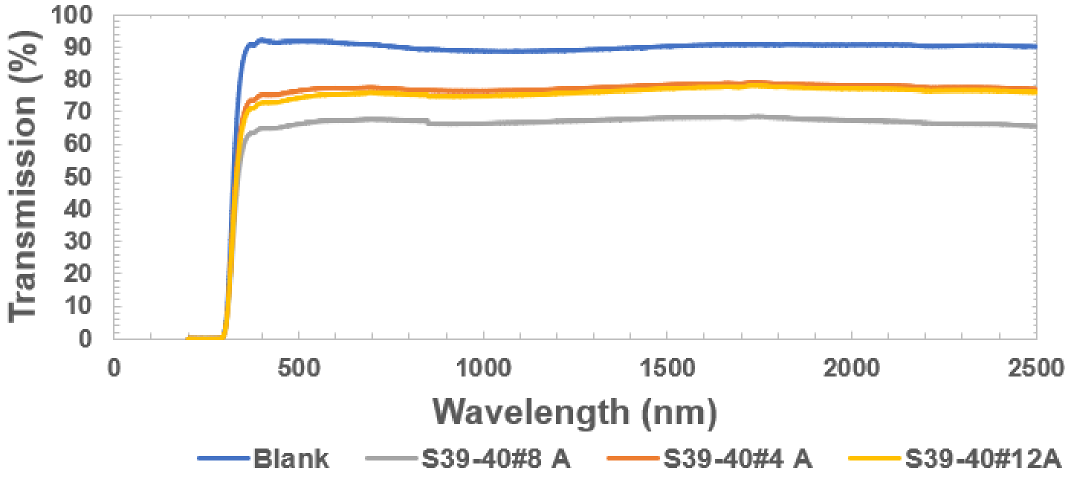


Figure 31 S39 Transmission - Vary Mayer rod

Figure 31 above shows transmission for synthesis 39 using the 3 different Mayer rods. Each curve is the average of two measurements at different parts of the slide.

5.3.3.3 Synthesis 28 Transmissivity

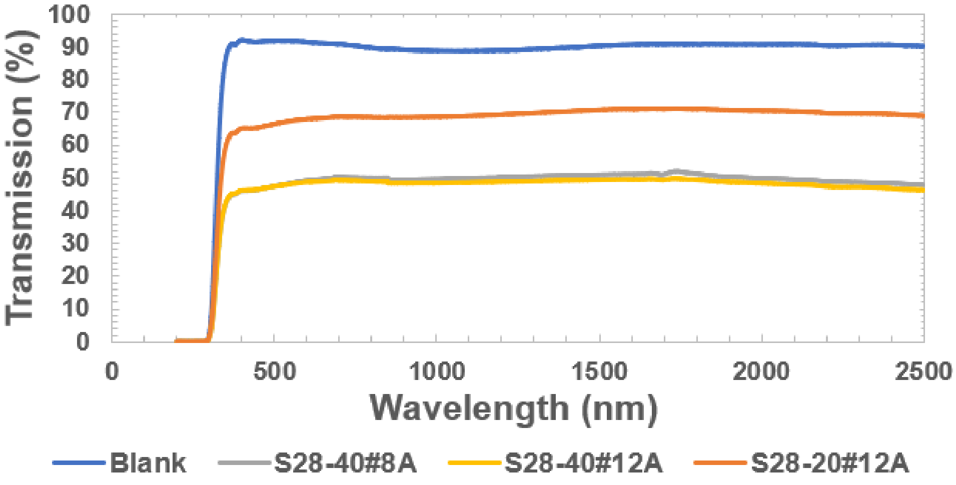


Figure 32 S28 Transmission

Figure 32 above shows synthesis 28 with variation of concentration and Mayer rods. Each curve is the average of two measurements at different parts of the slide.

5.3.3.4 Synthesis 5 Transmissivity

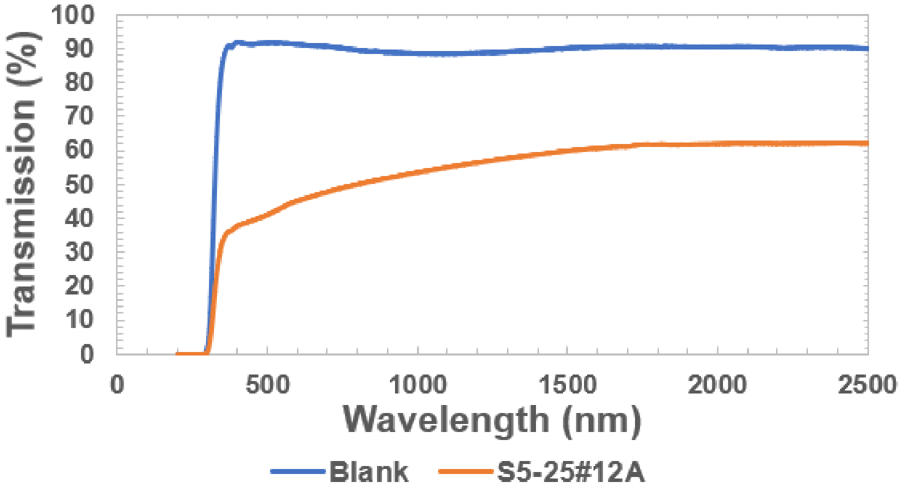


Figure 33 S5 Transmission

Figure 33 above shows the average transmission for synthesis 5 at two different parts of the slide.

5.4 Crystal Structure XRD

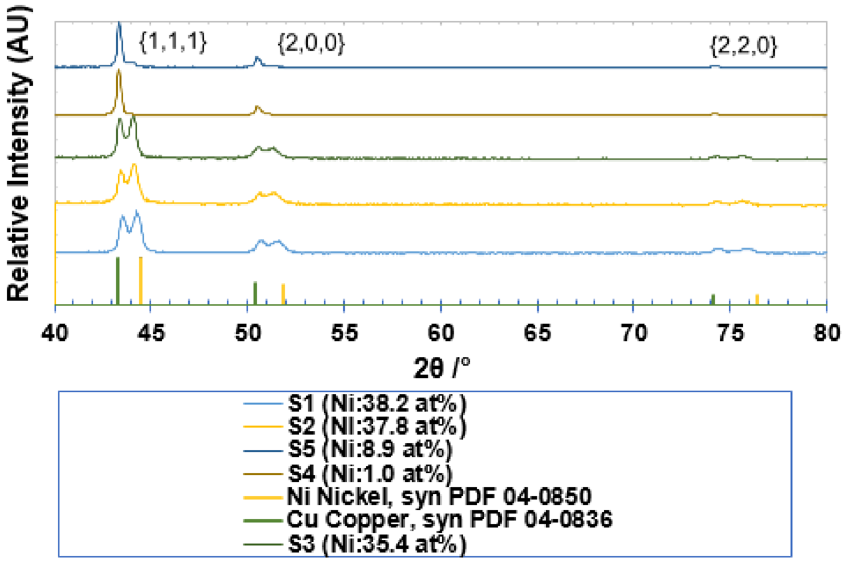


Figure 34 XRD Pattern of Syntheses 1 to 5

In Figure 34 above the curves have been separated from one another so that they do not overlay themselves. They are presented using relative intensity as they are being compared with each other. They are compared with the JCPDF database of nickel (04-0850) and copper (04-0836) shown in the bottom trace. There are 6 peaks between 40° and 80° that correspond to the data peaks. From the bottom trace, the LH peaks are copper and the RH nickel.

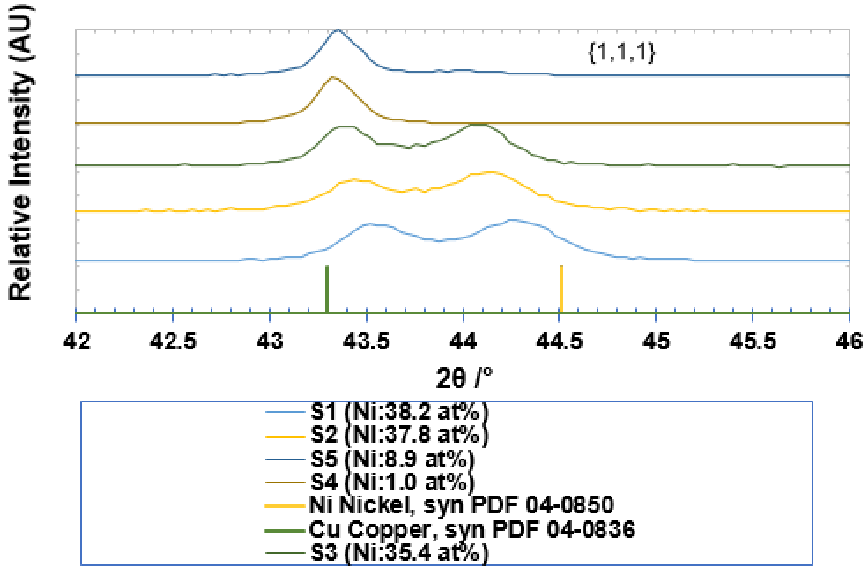


Figure 35 XRD Pattern Close Up

The curves are shown in more detail between 42° and 46° in Figure 35 for resolution and clarity.

5.5 During Synthesis Sampling

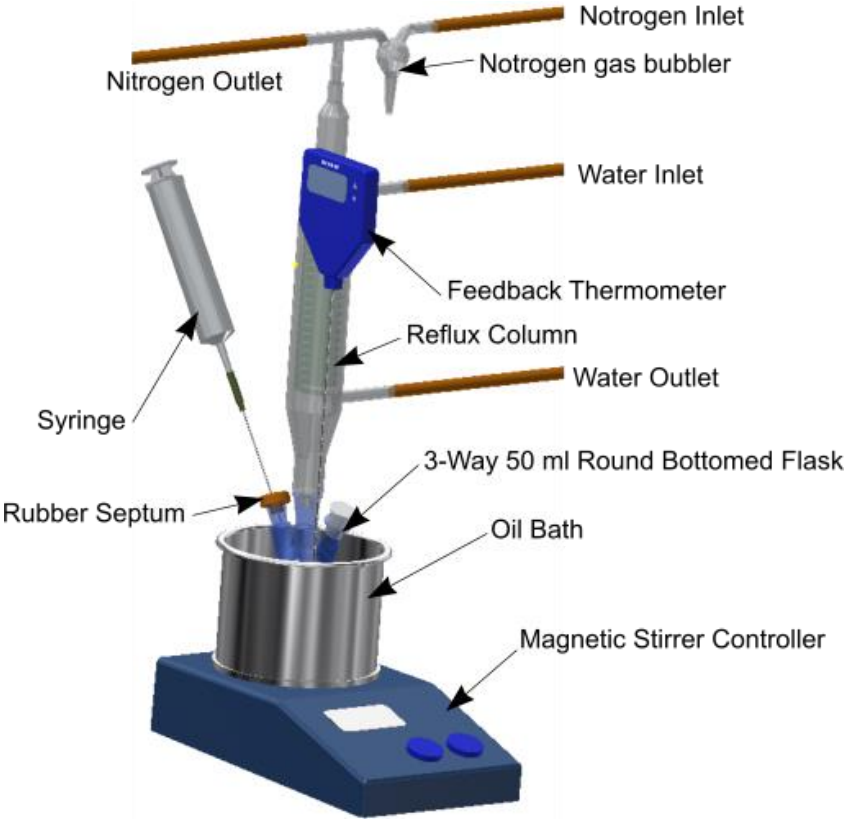


Figure 36 During Synthesis Sampling 3D Illustration

Figure 36 shows the setup for during synthesis sampling. The main part of this research was to systematically vary the chemical ratio’s and heat cycle to maximise the aspect ratio so as to optimise the optoelectronic properties of the nanowire layer whilst ensuring that it does not corrode. It is well known that copper can be grown anisotropically through a heat cycle in the presence of an alkylamine such as olyilamine. It is not however, completely understood why and how this occurs. It is assumed that the chemicals added to the mix, first grow nanoparticles isotropically, from which nanowires grow anisotropically over time. To try and capture this process, I changed the setup slightly to enable samples to be taken during synthesis.

5.5.1 During Synthesis Sampling Setup

The arrangement was kept the same, but the 50 ml round bottom flask was changed for one with more than one entrance. Only a three-entrance flask was available, so a glass stop was used to cover one entrance and a rubber septum to cover the other extra entrance. The rubber septum allows samples to be drawn during synthesis without compromising the atmospheric seal using a syringe. See Figure 36 for 3D drawings of setup.

5.5.2 During Synthesis Sampling Trial

This method was first tested during a normal synthesis to see if it worked, was possible and to find any problems. For this test, it was decided to start sampling early and regularly to find when it was first possible to detect any build-up of particles or wires. Although analysis hadn’t been done on synthesis 32, at the time, there appeared to be a good yield and under the optical microscope, the aspect ratio appeared better than normal. It was decided to repeat the synthesis, varying only the glucose content (synthesis 33), taking samples early on. This synthesis was conducted at 145 °C for around 17 hours with 0.6 g glucose. Of course, when taking samples during synthesis, the magnetic stirrer should be switched off first so as not to damage the syringe. The mixture was heated to 95 °C and held for 30 minutes to evacuate any water or oxygen present as normal. The mixture was then heated to 145 °C and the first sample taken (33A). The second sample was taken 20 minutes later when the stirrer was first switched off (33B). The final sample (33C) was taken 20 minutes later which was 20 minutes after the normal synthesis start time. The synthesis was continued overnight, and the product cleaned as normal (33).

5.5.2.1 During Synthesis Sampling Trial Results

As scrubbing or cleaning the nanowires normally takes around 5 hours for each sample, for economy, it was decided to superficially clean the samples taken during synthesis. The first sample taken (33A) was mixed with warm hexane and vortexed for 3 minutes before being spun in the centrifuge to separate any heavy metal parts from the mix for 25 minutes. Once settled, the supernatant extracted, and the process repeated with more hexane to clear away the dark oleylamine colour, but no sediment could be seen at all. Either the process had not started, or any particles were too small, too few or too light to be collectively seen with the naked eye.

This process was repeated for the next sample (33B) but this time a little residue could be seen. Once micrographs were taken using the SEM, neither nanowires nor nanoparticles could be seen, only what looked like different shaped conglomerates of contaminates.

The final sample (33C) was taken 20 minutes into the normal synthesis and this time after cleaning with hexane, it was possible to see a sediment and was cleaned further. Micrographs taken on the SEM are shown below; -

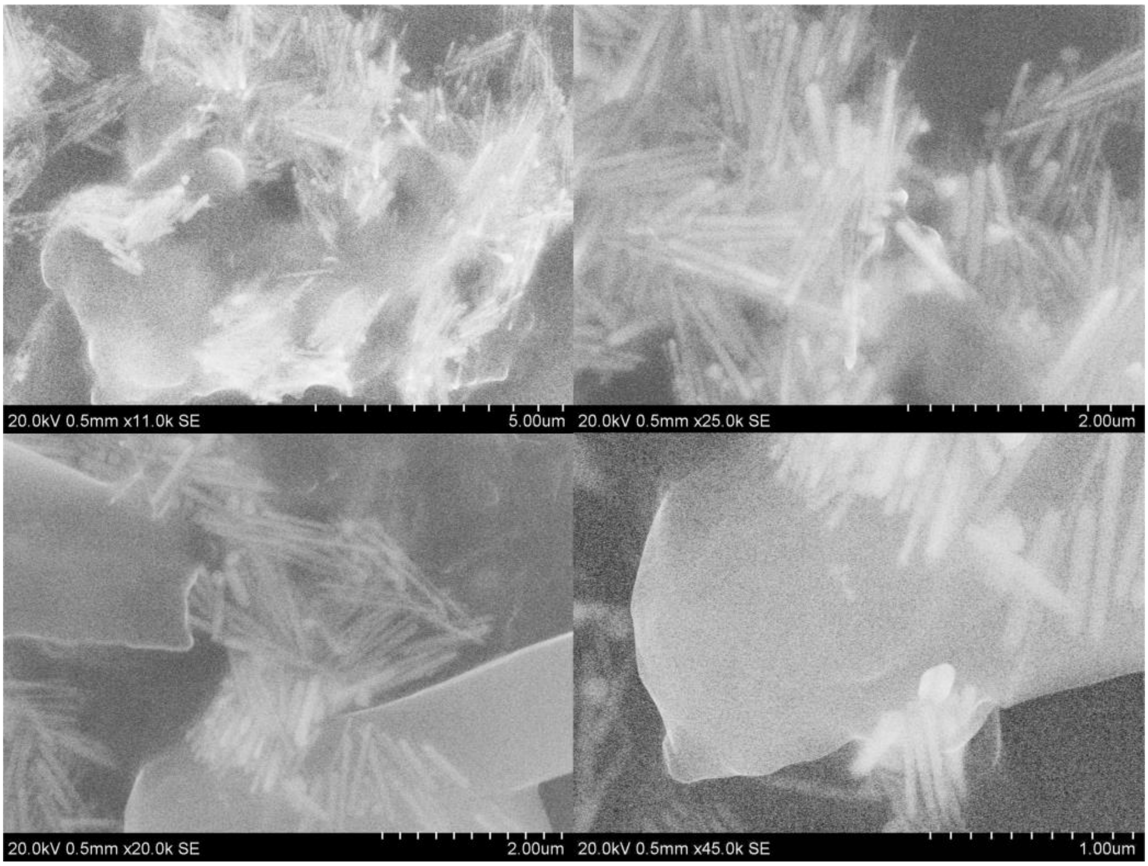
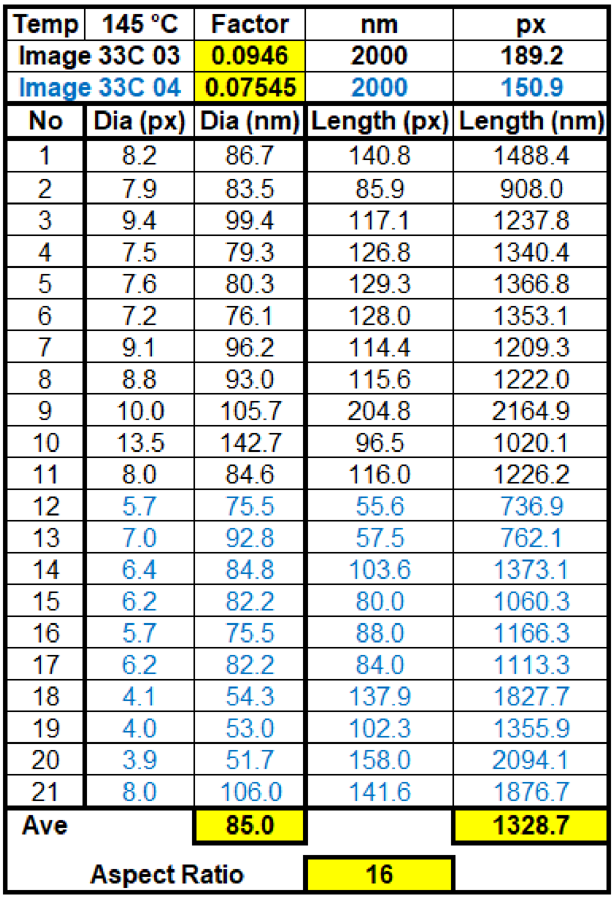


Figure 37 Micrographs of sample 33C

From the micrographs, measurements were taken using Inkscape 0.92 which gave the following results shown in Table 14; -



Temp	145 °C	Factor	nm	px
Image 33C 03		0.0946	2000	189.2
Image 33C 04		0.07545	2000	150.9
No	Dia (px)	Dia (nm)	Length (px)	Length (nm)
1	8.2	86.7	140.8	1488.4
2	7.9	83.5	85.9	908.0
3	9.4	99.4	117.1	1237.8
4	7.5	79.3	126.8	1340.4
5	7.6	80.3	129.3	1366.8
6	7.2	76.1	128.0	1353.1
7	9.1	96.2	114.4	1209.3
8	8.8	93.0	115.6	1222.0
9	10.0	105.7	204.8	2164.9
10	13.5	142.7	96.5	1020.1
11	8.0	84.6	116.0	1226.2
12	5.7	75.5	55.6	736.9
13	7.0	92.8	57.5	762.1
14	6.4	84.8	103.6	1373.1
15	6.2	82.2	80.0	1060.3
16	5.7	75.5	88.0	1166.3
17	6.2	82.2	84.0	1113.3
18	4.1	54.3	137.9	1827.7
19	4.0	53.0	102.3	1355.9
20	3.9	51.7	158.0	2094.1
21	8.0	106.0	141.6	1876.7
Ave		85.0		1328.7
Aspect Ratio			16	

Table 14 Sample 33C NW Aspect Ratio

Measurement numbers 1-11 shown in black, refer to measurements taken from image 33C 03 while numbers 12-21 shown in blue, to measurements taken from image 33C 04. The 2nd column (Dia px) and the 4th column (Length px) refer to the number of pixels in each measurement. The factor converts these pixels into nm and displays them in columns 3 and 5 respectively, headed Dia (nm) and Length (nm). The average Dia and Length is calculated at the bottom highlighted in yellow and shown in nm. The aspect ratio is calculated from these two values.

It is quite interesting to see when the nanowires start to grow, but also surprising that very few nanoparticles can be seen. It was expected that first nanoparticles would grow from nothing to a certain size, stop and then nanowires would grow from these particles.

Much was learnt from this first trial and modifications made to the process for the main, “during synthesis sampling” trials.

5.5.3 During Synthesis Sampling

As a large quantity of the mixture is required for each sample to be visible, after 3 samples (A, B & C), not much is left for the synthesis, so it was decided to abandon the synthesis after the third sample was taken and repeat the complete synthesis. This way, the synthesis should not be affected by the sampling and also it should show what would happen to the growth process if it would have completed. The abandoned first synthesis would also provide a fourth sample (D)

5.5.3.1 During Synthesis Sampling Results

Three samples were taken at various points during synthesis 37. Only three needles were available for sampling and also not much of the mixture is left after three samples have been taken so the process was abandoned an hour after the final sample (37C) was taken. This was called sample 37D. The same synthesis was then repeated in the normal 50 ml round flask and allowed to run its course overnight before being cleaned and analysed (synthesis 38). Syntheses 37 and 38 contained 0.5 g glucose at a temperature of 180 °C.

S39 samples were cleaned between a normal synthesis and the ones done during the trail. Each sample was cleaned with hexane until the solution became clear (two or three times), then once with acetic acid, once more with hexane and finally with once with IPA.

5.5.3.1.1 During Synthesis Sampling Results S37A

The first sample (37A) was taken at the very start of the synthesis process when the stirrer was switched off. No real particles or wires could be seen in the trial previously (S33) at this stage but because the temperature was higher, 180 °C rather than 145 °C it was mixing for longer before it finally got up to temperature.

Once cleaned, mainly nanoparticles could be seen but the start of a few nanowires were also present. See Table 15 below; -

Temp 180 °C	Factor	nm	px
Image 37A 01	0.03024	5000	151.2
Image 37A 02	0.0831	2000	166.2
	No	Dia (px)	Dia (nm)
	1	7.8	257.9
	2	10.2	337.3
	3	8.0	264.6
	4	8.0	264.6
	5	6.0	198.4
	6	6.0	198.4
	7	5.8	191.8
	8	6.8	224.9
	9	6.3	208.3
	10	6.4	211.6
	11	6.4	211.6
	12	6.4	77.0
	13	8.4	101.1
	14	10.3	123.9
	15	6.5	78.2
	16	16.1	193.7
	17	15.6	187.7
	18	10.5	126.4
	19	15.6	187.7
cube	20	19.0	228.6
cube	21	17.4	209.4
	Ave		194.4

Table 15 Sample 37A Nanoparticle Sizes

As in Table 14 measurements taken from different micrographs are shown in different colours in Table 15. Most of the NP's appeared with round edges except for the last two shown with "cube" written by the side of the measurements.

Temp	180 °C	Factor	nm	px
Image 37A 02		0.0831	2000	166.2
No	Dia (px)	Dia (nm)	Length (px)	Length (nm)
1	15.5	186.5	38.3	460.9
2	14.1	169.7	35.9	432.0
3	12	144.4	85.2	1025.3
4	12.4	149.2	99.2	1193.7
5	13.6	163.7	96.7	1163.7
6	7.9	95.1	47.2	568.0
7	14.4	173.3	81	974.7
Ave		154.5		831.2
	Aspect Ratio		5	

Table 16 Sample 37A NW Aspect Ratio

The average diameter of the nanoparticles measured is 194.4 nm which seems a little larger than expected for such an early sample, especially as they are larger than the average NW diameter. Table 16 shows the lengths and diameters of NW's from sample 37A that equate to an aspect ratio of just 5.

5.5.3.1.2 During Synthesis Sampling Results S37B

The second sample (37B) was taken 30 minutes after synthesis started. A micrograph of this sample is shown below in Figure 38; -

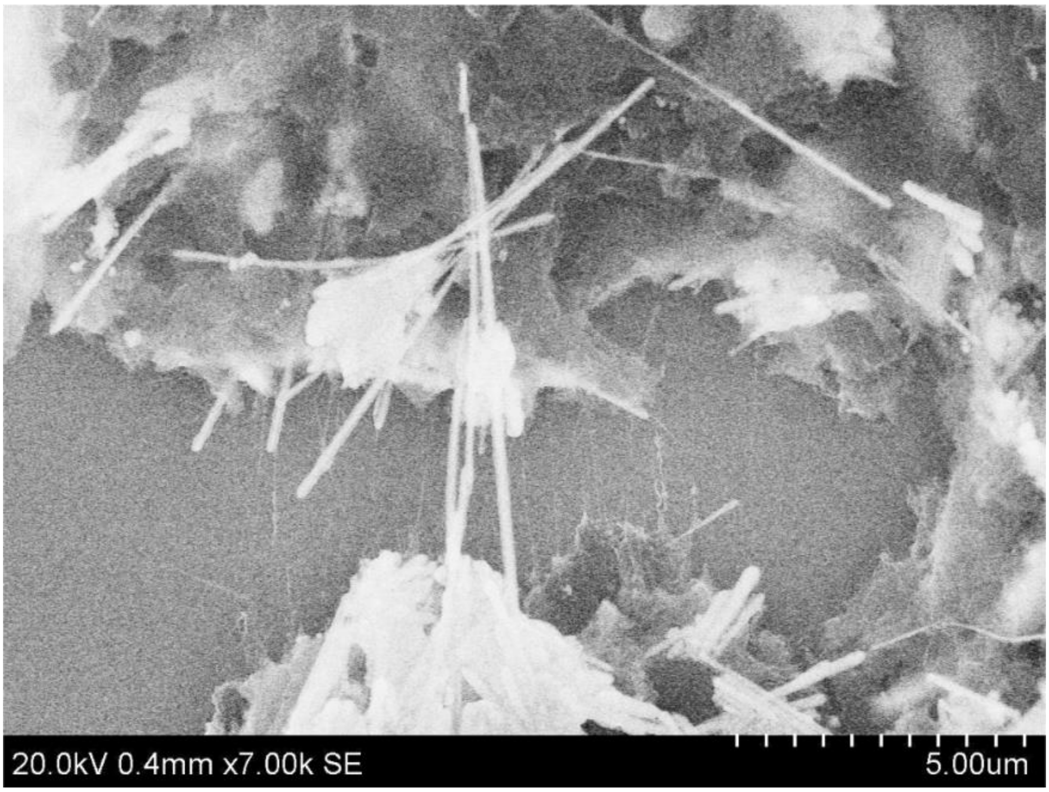
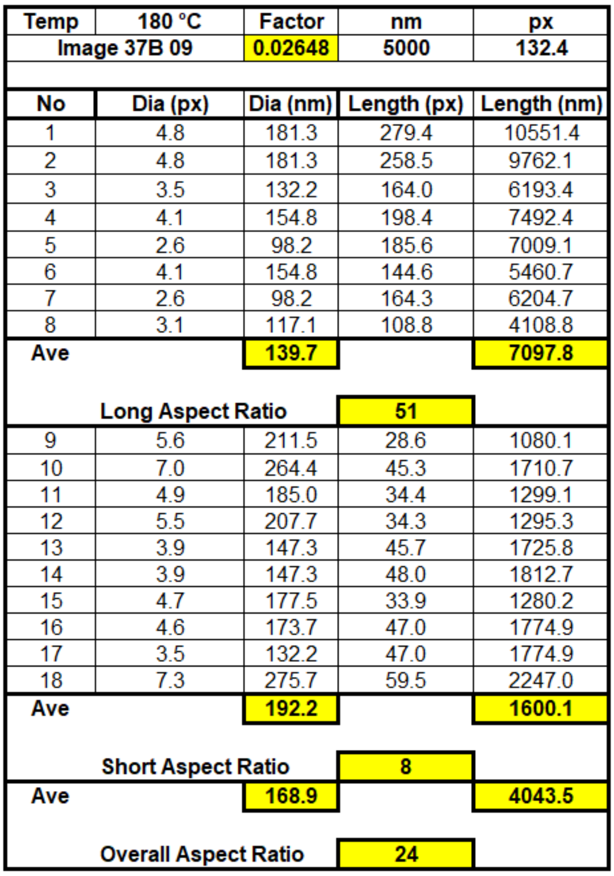


Figure 38 Sample 37B Micrograph

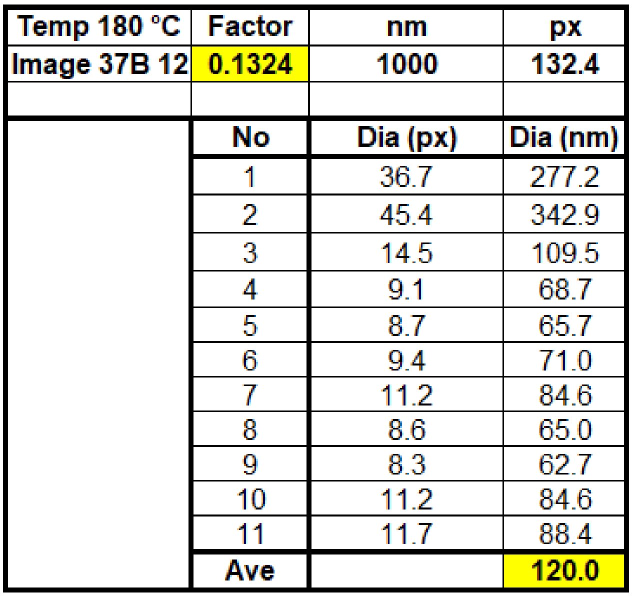
From this micrograph, it appears that there are two different clusters of NW's of differing lengths. Shorter ones gathered near the bottom, while longer ones near the middle and top. These two lengths are measured separately below in Table 17 with averages of each calculated before combining them at the bottom.



Temp	180 °C	Factor	nm	px
Image 37B 09		0.02648	5000	132.4
No	Dia (px)	Dia (nm)	Length (px)	Length (nm)
1	4.8	181.3	279.4	10551.4
2	4.8	181.3	258.5	9762.1
3	3.5	132.2	164.0	6193.4
4	4.1	154.8	198.4	7492.4
5	2.6	98.2	185.6	7009.1
6	4.1	154.8	144.6	5460.7
7	2.6	98.2	164.3	6204.7
8	3.1	117.1	108.8	4108.8
Ave		139.7		7097.8
Long Aspect Ratio			51	
9	5.6	211.5	28.6	1080.1
10	7.0	264.4	45.3	1710.7
11	4.9	185.0	34.4	1299.1
12	5.5	207.7	34.3	1295.3
13	3.9	147.3	45.7	1725.8
14	3.9	147.3	48.0	1812.7
15	4.7	177.5	33.9	1280.2
16	4.6	173.7	47.0	1774.9
17	3.5	132.2	47.0	1774.9
18	7.3	275.7	59.5	2247.0
Ave		192.2		1600.1
Short Aspect Ratio			8	
Ave		168.9		4043.5
Overall Aspect Ratio			24	

Table 17 Sample 37B NW aspect Ratio

There were also a few nanoparticles to be seen summarised below in Table 18;-



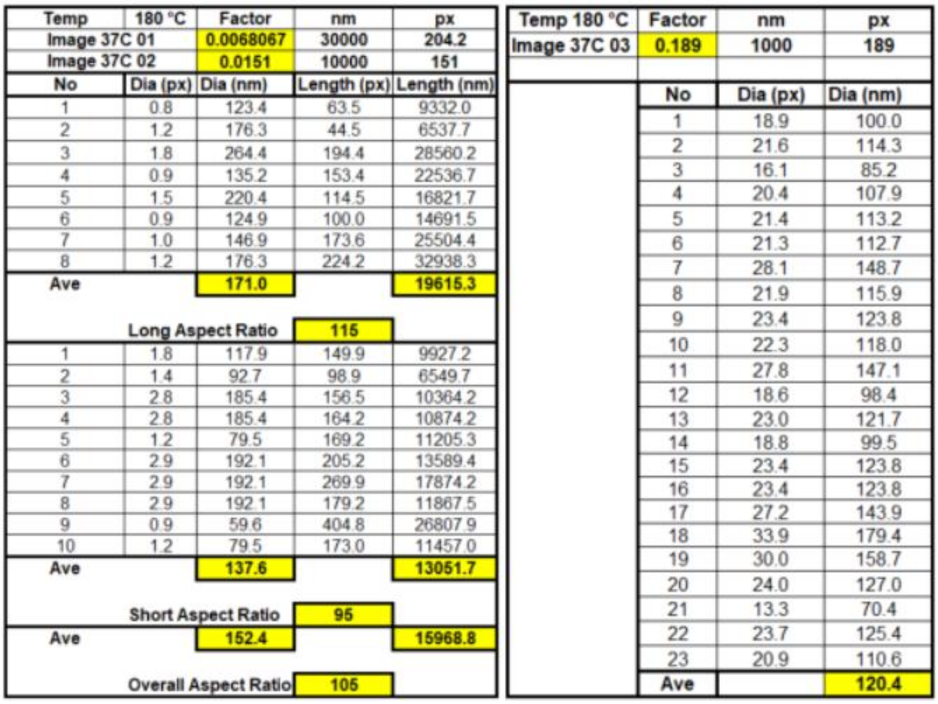
Temp 180 °C	Factor	nm	px
Image 37B 12	0.1324	1000	132.4
	No	Dia (px)	Dia (nm)
	1	36.7	277.2
	2	45.4	342.9
	3	14.5	109.5
	4	9.1	68.7
	5	8.7	65.7
	6	9.4	71.0
	7	11.2	84.6
	8	8.6	65.0
	9	8.3	62.7
	10	11.2	84.6
	11	11.7	88.4
	Ave		120.0

Table 18 Sample 37B Nanoparticle Sizes

This time, the average NP diameter seems to be smaller than any of the NW diameters shown in Table 17.

5.5.3.1.3 During Synthesis Sampling Results S37C

The third sample (37C) was taken an hour later than the second, 90 minutes after the start of the synthesis process. Table 19 summarises the NW's and NP's measured; -



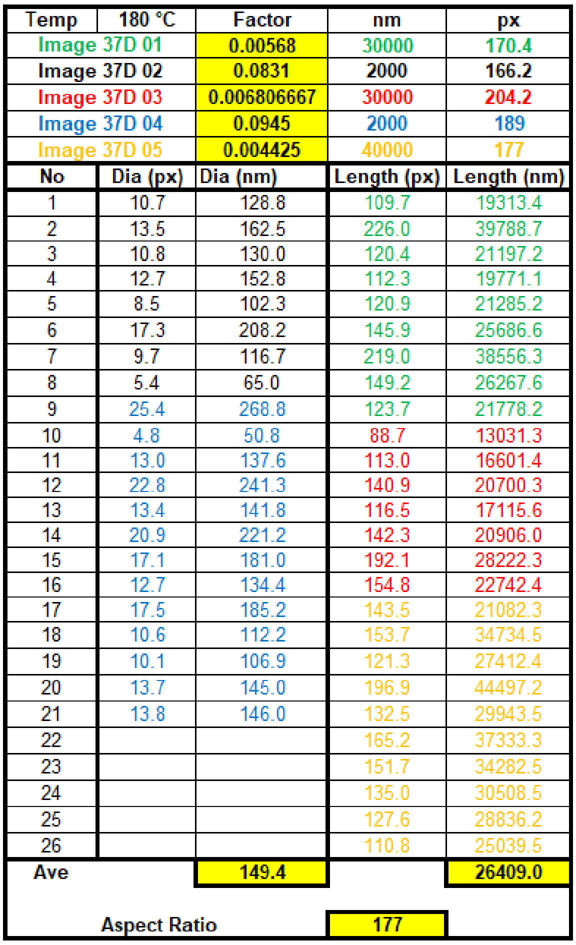
Temp	180 °C	Factor	nm	px
Image 37C 01		0.0068067	30000	204.2
Image 37C 02		0.0151	10000	151
No	Dia (px)	Dia (nm)	Length (px)	Length (nm)
1	0.8	123.4	63.5	9332.0
2	1.2	176.3	44.5	6537.7
3	1.8	264.4	194.4	28560.2
4	0.9	135.2	153.4	22536.7
5	1.5	220.4	114.5	16821.7
6	0.9	124.9	100.0	14691.5
7	1.0	146.9	173.6	25504.4
8	1.2	176.3	224.2	32938.3
Ave		171.0		19615.3
	Long Aspect Ratio		115	
1	1.8	117.9	149.9	9927.2
2	1.4	92.7	98.9	6549.7
3	2.8	185.4	156.5	10364.2
4	2.8	185.4	164.2	10874.2
5	1.2	79.5	169.2	11205.3
6	2.9	192.1	205.2	13589.4
7	2.9	192.1	269.9	17874.2
8	2.9	192.1	179.2	11867.5
9	0.9	59.6	404.8	26807.9
10	1.2	79.5	173.0	11457.0
Ave		137.6		13051.7
	Short Aspect Ratio		95	
Ave		152.4		15968.8
	Overall Aspect Ratio		105	

Temp 180 °C	Factor	nm	px
Image 37C 03	0.189	1000	189
	No	Dia (px)	Dia (nm)
	1	18.9	100.0
	2	21.6	114.3
	3	16.1	85.2
	4	20.4	107.9
	5	21.4	113.2
	6	21.3	112.7
	7	28.1	148.7
	8	21.9	115.9
	9	23.4	123.8
	10	22.3	118.0
	11	27.8	147.1
	12	18.6	98.4
	13	23.0	121.7
	14	18.8	99.5
	15	23.4	123.8
	16	23.4	123.8
	17	27.2	143.9
	18	33.9	179.4
	19	30.0	158.7
	20	24.0	127.0
	21	13.3	70.4
	22	23.7	125.4
	23	20.9	110.6
	Ave		120.4

Table 19 Sample 37C Nanowires and Nanoparticles

5.5.3.1.4 During Synthesis Sampling Results S37D

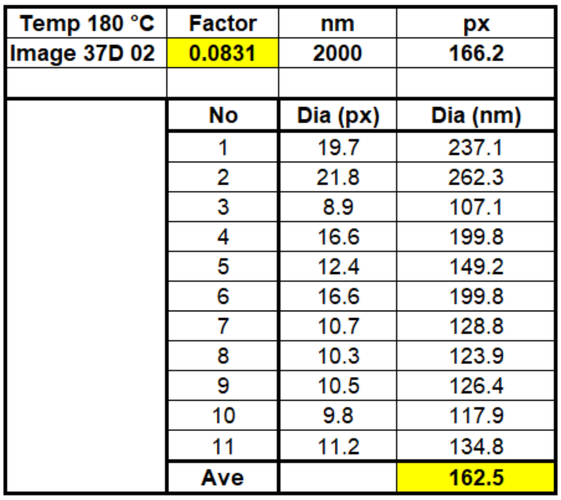
The final sample was not taken using the syringe, rather the process was stopped prematurely after 90 minutes.



Temp	180 °C	Factor	nm	px
Image 37D 01		0.00568	30000	170.4
Image 37D 02		0.0831	2000	166.2
Image 37D 03		0.006806667	30000	204.2
Image 37D 04		0.0945	2000	189
Image 37D 05		0.004425	40000	177
No	Dia (px)	Dia (nm)	Length (px)	Length (nm)
1	10.7	128.8	109.7	19313.4
2	13.5	162.5	226.0	39788.7
3	10.8	130.0	120.4	21197.2
4	12.7	152.8	112.3	19771.1
5	8.5	102.3	120.9	21285.2
6	17.3	208.2	145.9	25686.6
7	9.7	116.7	219.0	38556.3
8	5.4	65.0	149.2	26267.6
9	25.4	268.8	123.7	21778.2
10	4.8	50.8	88.7	13031.3
11	13.0	137.6	113.0	16601.4
12	22.8	241.3	140.9	20700.3
13	13.4	141.8	116.5	17115.6
14	20.9	221.2	142.3	20906.0
15	17.1	181.0	192.1	28222.3
16	12.7	134.4	154.8	22742.4
17	17.5	185.2	143.5	21082.3
18	10.6	112.2	153.7	34734.5
19	10.1	106.9	121.3	27412.4
20	13.7	145.0	196.9	44497.2
21	13.8	146.0	132.5	29943.5
22			165.2	37333.3
23			151.7	34282.5
24			135.0	30508.5
25			127.6	28836.2
26			110.8	25039.5
Ave		149.4		26409.0
	Aspect Ratio		177	

Table 20 Sample 37D NW Aspect Ratio

Table 20 above shows sample 37 NW details and Table 21 below shows NP details.

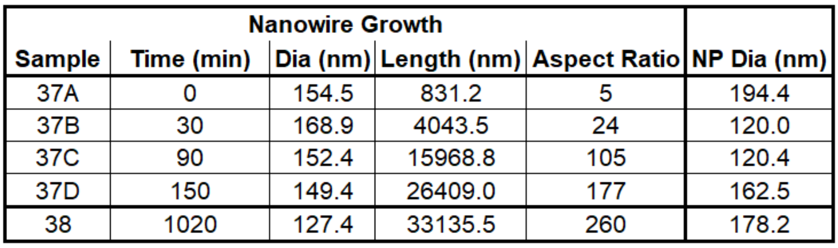


Temp 180 °C	Factor	nm	px
Image 37D 02	0.0831	2000	166.2
	No	Dia (px)	Dia (nm)
	1	19.7	237.1
	2	21.8	262.3
	3	8.9	107.1
	4	16.6	199.8
	5	12.4	149.2
	6	16.6	199.8
	7	10.7	128.8
	8	10.3	123.9
	9	10.5	126.4
	10	9.8	117.9
	11	11.2	134.8
	Ave		162.5

Table 21 Sample 37D Nanoparticles

5.5.3.1.5 During Synthesis Sampling Results Summary

The results of the four samples taken during synthesis 37 including synthesis 38 where the process was allowed to continue as normal to completion are shown below in Table 22; -



	Nanowire Growth				
Sample	Time (min)	Dia (nm)	Length (nm)	Aspect Ratio	NP Dia (nm)
37A	0	154.5	831.2	5	194.4
37B	30	168.9	4043.5	24	120.0
37C	90	152.4	15968.8	105	120.4
37D	150	149.4	26409.0	177	162.5
38	1020	127.4	33135.5	260	178.2

Table 22 Growth During Synthesis Summary

6 DISCUSSION

As much as possible, the heading titles will follow the heading titles for the results. So, for example, “The results for Copper-Nickel nanowire synthesis – High temperature – vary glucose” from the results in section 5.1.1 will be discussed in section 6.1.1 in the discussion.

6.1 Copper-Nickel Nanowire Synthesis

6.1.1 High Temperature – Vary Glucose

Initially, the 195 °C temperature could not be reached, the system really struggled to get above 190 °C so a foil reflective lid was made which solved the problem. This was first tried on synthesis 5 so the temperature was set to 190 °C rather than 195 °C so that it would be closer to the actual synthesis temperatures of syntheses 1 to 4. The first 3 syntheses varied the glucose between 0.25, 0.5 and 1.0 g of glucose which all gave nickel contents of 35% plus, so it was unnecessary to try 0.75 g glucose. I therefore tried less than 0.25 g to lower the nickel content to between 5 – 20%. Synthesis 4 halved the glucose to 0.125 g which had a nickel content of around 1%. An intermediate synthesis 5 was made with 0.2 g glucose which produced NW’s with about 9% nickel. It was also noticed that the aspect ratio increased from less than 200 in the first 3 syntheses to almost 800 in the 5th synthesis. These were very encouraging results, it looked like when the nickel content was what we require, the aspect ratio peaks.

Figure 15 implies that the aspect ratio peaks around 0.2 g glucose when the synthesis temperature is high.

Figure 16 shows that when the glucose is varied from 0 to 1 g, the Ni content rises sharply at about 2 g, reaches a peak of around 38% nickel at about 0.3 g glucose.

When there are not many data points, less reliable curves result, and it is possible that this is not a true trend. In all results I have plotted curves joined by solid straight or curved lines for clarity. They do not mean that other intermediate points necessarily follow these curves.

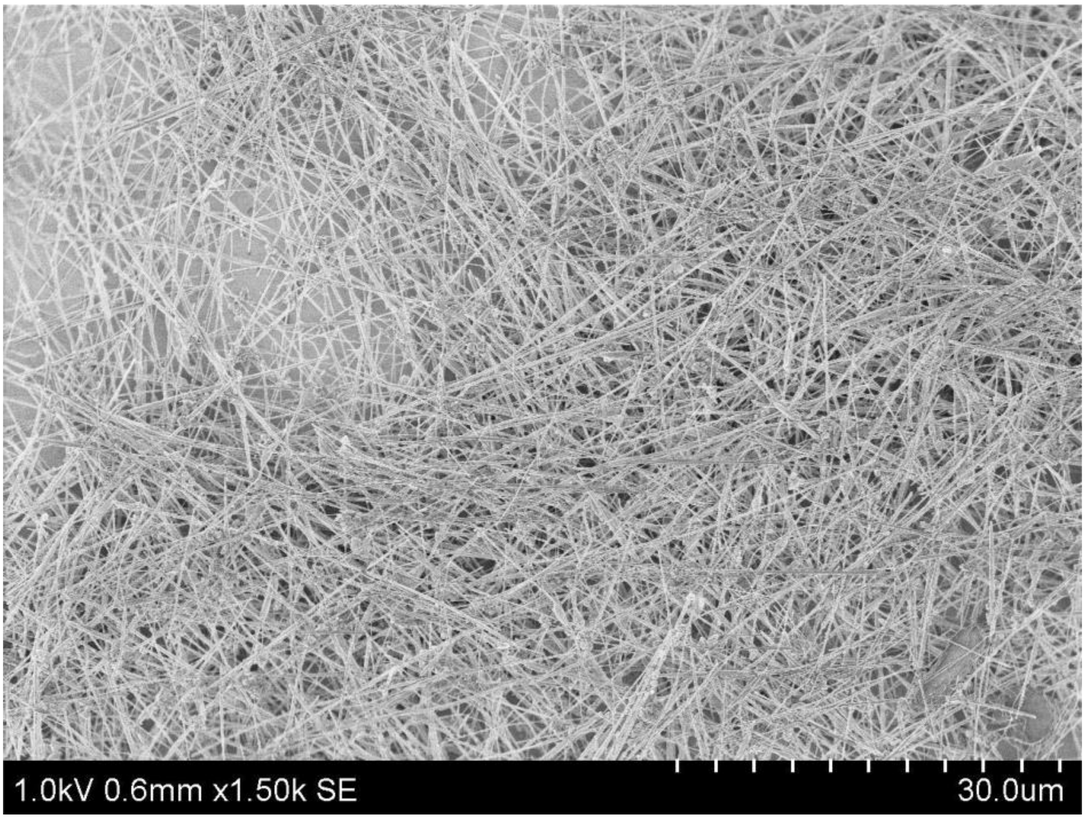
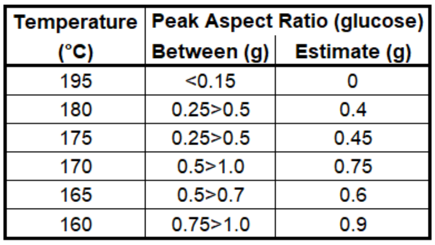


Figure 39 Synthesis 5 NW Micrograph

Figure 39 shows a micrograph of quite respectable nanowires taken at 1500 times magnification of synthesis 5 having a good aspect ratio (788) and nickel content (8.9% Ni). Very little bundling or contamination appears present.

6.1.2 Lower Temperature – Vary Glucose

From Figure 17, although there are not enough points, the results do seem to follow a trend. Looking at the orange 175 °C for example, a peak appears somewhere between the 0.25 g and 0.5 g glucose data points. From the curve, it looks like the actual peak should be around 0.45 g glucose. Doing the same thing for the other temperatures, Table 23 summarises these estimates.



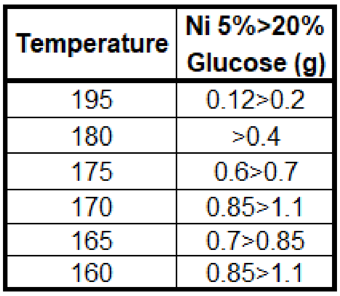
Temperature (°C)	Peak Aspect Ratio (glucose)	
	Between (g)	Estimate (g)
195	<0.15	0
180	0.25>0.5	0.4
175	0.25>0.5	0.45
170	0.5>1.0	0.75
165	0.5>0.7	0.6
160	0.75>1.0	0.9

Table 23 Aspect Ratio - Vary Temperature

The glucose content of the peak aspect ratio seems to increase as the temperature is reduced. The obvious exception to this rule is 170 °C where the result would be expected to have been between 175 °C (0.5 g) and 165 °C (0.6 g). If the 0.5 g point is incorrect and it was higher, then the curve could peak somewhere between 0.45 - 0.6

g glucose. This synthesis was repeated (synthesis 20), once it was found that others had used the equipment but very similar results were obtained for both aspect ratio and nickel content so it didn't solve the problem.

Figure 18 also appears inconsistent at first sight. The 195 °C curve, shown in Figure 16 showed that the nickel content started small and suddenly rose to around 35% and stabilised. The glucose content at this rise was around 0.25 g. It may be that the glucose level was not high enough to see this rise and stability part of the curve. In fact, most of the other curves do appear to rise sharply towards the highest glucose contents. It could be that to obtain 35% nickel in the wires at lower temperatures requires more glucose. However, we are not really interested in that part of the curves - as long as we can get between 5 – 20% nickel content we fulfil the second aim.



Temperature	Ni 5%>20% Glucose (g)
195	0.12>0.2
180	>0.4
175	0.6>0.7
170	0.85>1.1
165	0.7>0.85
160	0.85>1.1

Table 24 Ni Content - Vary Temperature

A similar trend becomes clear when looking at estimates of when the nickel content is between 5%>20% in Table 24. As the temperature is lowered, the glucose necessary for Ni between 5>20% increases. Again, the exception is for the 170 °C syntheses 15 and 20.

6.1.3 First Aim – Increase Aspect Ratio > 400

The molar concentration of copper II chloride dihydrate should be twice that of the nickel II acetate tetrahydrate for maximum efficiency. However, because some of the nickel is being incorporated into the wires, not all of it is being used as a catalyst so it might require a higher concentration of Ni to maintain the best efficiency. It was decided to test this theory by repeating synthesis 21 with a higher percentage in synthesis 22. Because 10% is a reasonable aim for the nickel content, the nickel compound was increased by 10% to 0.3285 g. The results are shown in Table 25 below: -

No	Mass (g) Glucose	Temp (°C)	$Ni(C_2H_3O_2)2.4H_2O$ (g)	SEM Observations				No
				Ø Ave (nm)	L Ave (µm)	Aspect	(%at.)	
21	0.5	160	0.2986	129.9	21.9	168	2	21
22	0.5	160	0.3285	92.5	30.9	334	0	22

Table 25 Increase Nickel Compound

The nickel content hardly changed but the aspect ratio almost doubled. It was a little unexpected that the nickel content went down when it was increased in the mix. As this small increase seemed to have such an effect on the aspect ratio, this value was therefore used on all subsequent syntheses (syntheses 22 to 40).

From Table 8 the 0.75 g glucose highlighted in red are the syntheses that used this new weight of the Ni compound (0.3285 g). The curve seen in Figure 19 looks quite symmetrical but a smaller peak at each side of the main peak are present. These could be because there are not enough measurements taken but more data points would be necessary to confirm. The main peak occurs just over 900 aspect ratio between 140-150 °C. To keep the best aspect ratio while producing NW’s within the 5-20% Ni content range, 160 °C would be the choice when using 0.75 g glucose.

6.1.4 Second Aim – Optimise Nickel Content

Table 9 shows varying glucose syntheses at 160°C. Typical of research, the 0.75 g glucose synthesis contained no Ni but 1 and 1.25 g glucose were both within the range. The synthesis numbers are 19 and 39 but 19 had an aspect ratio of <200 while 39 over 500. Therefore synthesis 39 was chosen for the main optoelectronic tests.

6.2 Curing

6.2.1 Heat Curing

Before heat curing the slides must be checked on an optical microscope for good percolation to obtain a conductive surface. As long as there is percolation it should be conductive. The only exception was when putting two slides in the tubular oven together and neither was conductive. The samples must be placed in the centre of the tubular oven to work. For the results of the conductivity tests see 5.3.2 and for discussion 6.3.2.

6.2.2 UV Curing

Plenty of time and effort was spent trying to get the UV curing method working without success. To start with, it was thought that the NW's had not been cleaned enough so that problem was solved. Then it was suspected that it was the presence of Ni that caused the problem, so syntheses were tried that contained no Ni. This only really left the bulb that could be a problem. The bulb was replaced for a new one but the problem remained and time was short so all the samples had to be cured by heat treatment which takes considerably longer (around 7 hours opposed to 2 minutes). The only difference between syntheses when growing pure Cu NW's and CuNi ones is the addition of glucose. It is possible that a reaction with the glucose somehow creates an insulating layer between the NW's which requires high temperatures to remove.

6.3 Optoelectronic Testing

6.3.1 Inks

Various inks were prepared with varying concentrations of NW's to solution. These were all initially spread using the #12 Mayer rod to give the thickest coat and in some further cases using the #8 and #4 Mayer rods for comparison. It was found that some of the inks made earlier appeared to have dried considerably so the concentrations would be greater than intended but also unknown. From this point onwards, all inks made were sealed using Parafilm. Alternatively, NW's were allowed to dry, weighed and then sealed with Parafilm until an ink was required. In practice, not all syntheses are required to be made into inks, so this is probably the most efficient method. Also, it makes calculating the concentration easier. If you already have an ink that is 40 mg/ml and you want to dilute it to 30 mg/ml, the dilution necessary is not immediately obvious. Figure 23 shows the main values to be used.

6.3.1.1 Calculating Ink Dilution from 40 mg/ml Concentration

LET

V = volume of ink in ml

V_s = volume of solution required for dilution

C = concentration of produced ink at 40 mg/ml

C_s = concentration of desired solution

When V = 1 ml,

$C_s = C / (V+V_s) = 40 / (1+V_s)$ ---- Equation 8

To produce a given concentration C_s by altering V_s

If $C_s = 40 / (1+V_s)$ then

$V_s = (40 / C_s) -1$ --- Equation 9

Test: If 30 mg/ml is required to be diluted from 40 mg/ml ink, then

$V_s = (40/30) -1 = 1/3$ ml of solution should be added to 1 ml of 40 mg/ml original ink.

6.3.2 Resistance Testing

6.3.2.1 Syntheses 1-5 Resistance

The resistivity measurements were taken over about a month in free air at ambient temperature (around 20 °C).

From Table 10 and Figure 24, Synthesis 5 has the lowest resistance and appears to have stayed reasonably constant, although there may be signs of an increase towards the end. However, one last measurement was taken of this sample at the end of the research. The resistance was 1.95 Ω/□, the same as the very first measurement 112 days earlier and 49 of these days were stored at 50 °C. All the values were an average of 3 measurements. S5 has a Ni content of 8.9% and an aspect ratio of 788. From Table 10 it also has a very low resistivity of between 2 and 7 Ω/□. It certainly looks as if the sample will not oxidise over the lifetime of the product. The next lowest is S4 which also seems to have remained fairly stable over the month (30-45 Ω/□). This has a Ni content of 1% and an aspect ratio of 370. Syntheses 1 and 3 have similar resistance, both starting and finishing at a similar value. They both have a Ni content over 30 but only poor aspect ratios of 173 and 92 respectively, that's why they are the highest resistance.

It has been found that, according to where the 4 point probe is placed, the resistance varies considerably. For this reason, most resistance results were taken in 3 different places, recorded and averaged.

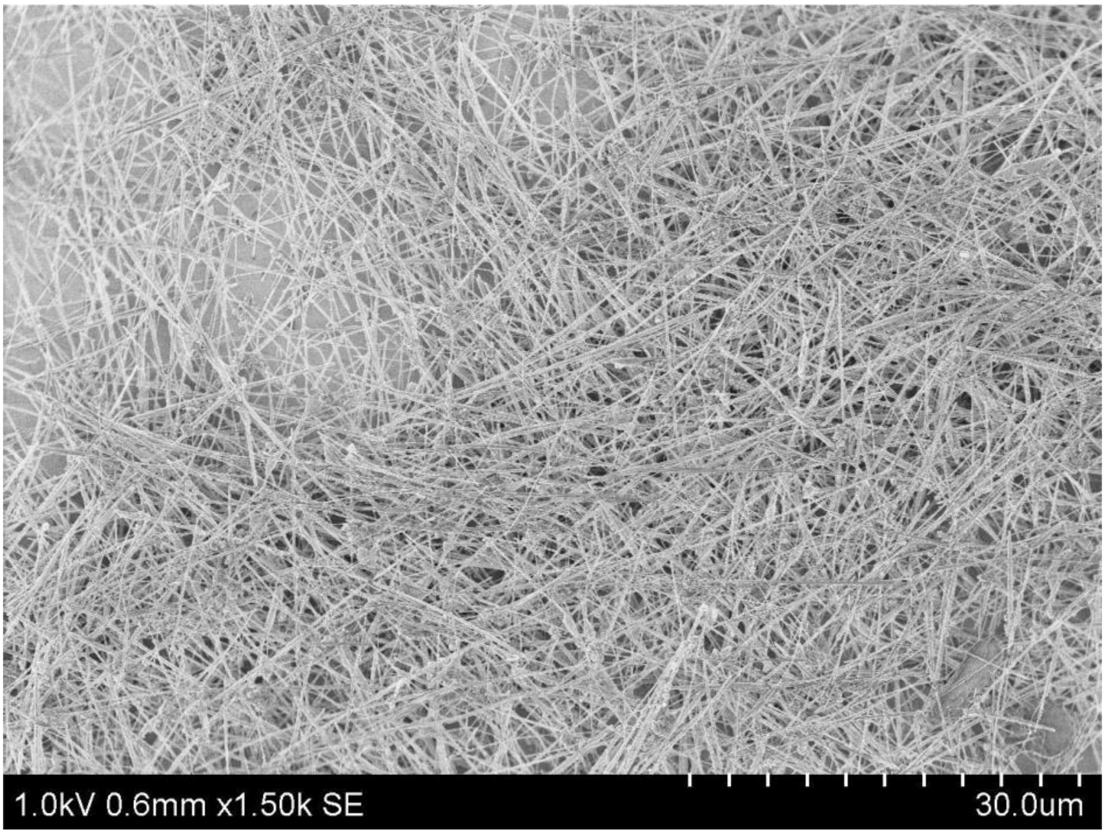


Figure 40 Synthesis 5 Micrograph

Synthesis 5 seems to have met all but aim 4. Aim 1 Increase aspect ratio to >400; S5 = 788. Aim 2 Control Ni content between 5% -20%; S5 = 8.9% Ni. Aim 3a optimist resistivity / transparency; S5 = 2-7Ω/□ / 60%.

6.3.2.2 Synthesis 39 Resistance

Looking at Figure 25, only S39-20 #12 sample is fairly stable, the others seem to be more random. I don't think that this is to do with oxidation, but uneven coating spread by the Mayer rods. If the NW coating is uneven, then sometimes the 3 point probe is over a thick conductive part and others over a thin high resistance part. When each slide is tested with the 4 point probe, the slide is moved near the centre and clamped. If it's non-conductive, it's moved until a stable reading is obtained. Once the values have been recorded between 0.1 and 1 mA, the slide is unclamped and moved slightly for the next readings. The next time the same slide is measured, it will be in a different place and could give completely different measurements. Although all reading have had higher measurements than the first ones, all of them are lower for the last measurement than the first, so it is unlikely to be oxidising with time.

6.3.2.3 Synthesis 28 Resistance

Looking at Figure 26, 40 #8 seems to vary the most and the coating on the slide does look uneven. The 20 #12 and 40 #12 slides look reasonably stable and it would be expected that the 40 mg/ml concentration would be more conductive than the 20 #12 coating. There was not really enough time to test these coatings. It was always expected that the UV curing would work once the new bulb arrived, so little time remained for heat treatments. When coating the PET with the Mayer rod, it seemed easier to get a consistent even coating than when using the glass slides. Glass has less friction and only 15 mm wide where the PET is cut much wider and does not skid. Using a Mayer rod to make the coating is cheap, quick and easy but the process was patented by Charles Mayer in 1912 so the process is over 100 years old and superseded by many modern methods.

6.3.3 Transmission Testing

6.3.3.1 Synthesis 1 Transmissivity

From Figure 27 the top red trace is plain blank glass without a coating that is used as a reference. Between about 500 and 200 nm it transmits around 90% of the light and so blocks out around 10%. The second green trace is the glass slide coated with NW’s using the #4 Mayer rod etc. This means that the #4 coating reduces the transmission by around another 10%.

From Figure 28 the ITO curve cannot go outside of the plain glass slide profile. It gives better transmission than the #4 Mayer rod with CuNi NW’s in two places only, between 300-500 nm and 800-1000 nm. The rest of the #4 curve is more transmissivity, especially in the ultraviolet. Also, these curves are for synthesis 1 which only has an aspect ratio of around 170. The optoelectronic properties are expected to be better for higher aspect ratios.

6.3.3.2 Synthesis 39 Transmissivity

Figure 31 shows the same concentration of ink (40 mg/ml) using the 3 different Mayer rods, #12, #8 and #4 against a clean blank glass slide. The blank glass transmits around 90% between 300 – 2500 nm. As Mayer rod #12 lays the thickest film, it would be expected to transmit the least light, followed by the #8 and the #4 would be expected to transmit the most as it’s the thinnest layer. Indeed, the #4 does transmit the most light at around 70% (80% of the blank) but it’s very closely followed by the #12 where the lowest transmission it from the #8 Mayer rod at around 60% (70% of the blank). Again, this is probably caused by the difficulty of an even spread across narrow glass slides.

6.3.3.3 Synthesis 28 Transmissivity

Figure 32 shows varying concentrations and thicknesses of synthesis 28 against a blank glass slide. This time the lowest concentration of ink (20 mg/ml) does transmit the most light at around 70% (80% of the blank) but the other two curves with different Mayer rods and 40 mg/ml concentration, transmit around the same at 50% (60% of the blank).

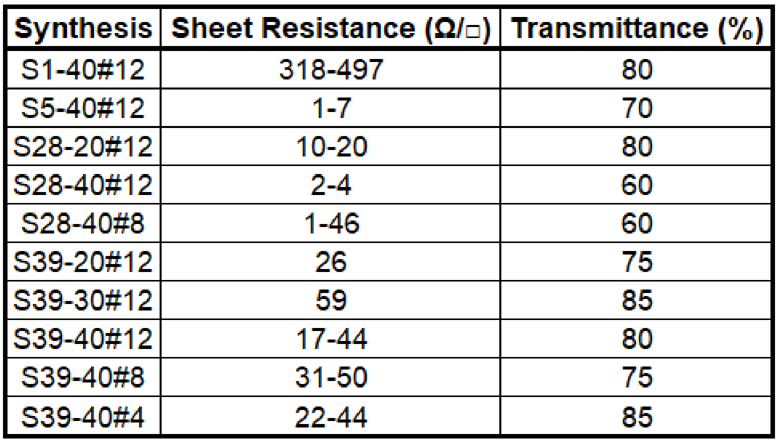
6.3.3.4 Synthesis 5 Transmissivity

Figure 33 shows the single curve of synthesis 5 against the blank glass which only transmits around 50% (60% of the blank) of the light but it seems to fall off at the smaller wavelengths. The concentration of this ink is 25 mg/ml so it would be expected to have been better at transmitting light than is was.

However, it can be seen from Figure 41 that this slide is very dark and unevenly spread. The ink concentration needs diluting considerably.

Figure 41 S5 Cured Slide

6.3.4 Optoelectronic Properties



Synthesis	Sheet Resistance (Ω/□)	Transmittance (%)
S1-40#12	318-497	80
S5-40#12	1-7	70
S28-20#12	10-20	80
S28-40#12	2-4	60
S28-40#8	1-46	60
S39-20#12	26	75
S39-30#12	59	85
S39-40#12	17-44	80
S39-40#8	31-50	75
S39-40#4	22-44	85

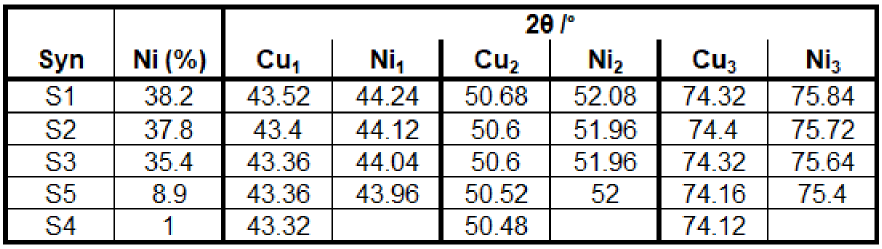
Table 26 Optoelectronic Properties Summary

Table 26 shows a summary of the collected data for both sheet resistance and transmittance. The numbers are rounded and transmittance shows the percentage below blank glass rather than absolute. A range of numbers in sheet resistance indicates measurements over time.

Some of the slides were very dark (S28-40 and S5) require both dilution and using a lower number Mayer rod to allow more light through. Of course, it's a compromise, if the coating is thinner and lets more light through then it will not be as conductive. Looking at Table 26, the best optoelectronic ink is S39-40#4 which had a range of sheet resistance between 22-44 Ω/□ and a transmittance of around 85%. As ITO is generally considered to be transparent in the visible to over 80% with a sheet resistance of around 15 Ω/□, our best result is definitely comparable to the standard reference we are trying to replace. However, because time was short at the end of this research because of problems encountered, more work is necessary to optimise the optoelectronic properties of the inks.

6.4 Crystal Structure XRD

Figure 35 is a magnified view of Figure 34 which will be used in this section. From Table 1 Cu has a cubic lattice structure of 361 pm on the side and Ni of 352 pm. There are three groups of two peaks at around 43.4°, 50.5° and 74.3° which correspond to the {1,1,1}, {2,0,0} and {2,0,2} planes of Cu metal. The double peaks can be seen clearer on the S1, S2 and S3 curves because they all have over 35% Ni content. The second, peak in each case represents the Ni. A little higher at 44 for {1,1,1}. The blue S5 trace has 8.9% Ni while the green S4 trace has 1% Ni. Comparing these peaks with the bottom trace for pure Cu and pure Ni, it can be seen that they are slightly offset. This shows that the NW's are an alloy of the two rather than separate. Each curve lies slightly towards the other metal. Looking closely at Figure 35, the curves containing less Ni are slightly closer to the bottom pure Cu peak. A table of peak values is taken from the data and presented below in Table 27.



		2θ /°					
Syn	**Ni (%)**	**Cu_1**	**Ni_1**	**Cu_2**	**Ni_2**	**Cu_3**	**Ni_3**
S1	38.2	43.52	44.24	50.68	52.08	74.32	75.84
S2	37.8	43.4	44.12	50.6	51.96	74.4	75.72
S3	35.4	43.36	44.04	50.6	51.96	74.32	75.64
S5	8.9	43.36	43.96	50.52	52	74.16	75.4
S4	1	43.32		50.48		74.12	

Table 27 Peak Values

As there are no other diffraction peaks there cannot be any other crystalline structures present.

6.5 During Synthesis Sampling

6.5.1 During Synthesis Sampling Setup

The syringe used was quite stiff so it was necessary to support the equipment when inserting and withdrawing.

6.5.2 During Synthesis Sampling Trial

6.5.2.1 Results

If samples taken are small or taken early, it is not possible to see any residue at the bottom of the flask after the centrifuge. The first sample where residue could be seen was S33B which was taken at time = 0 when the stirrer is first switched off. This time may be earlier if the synthesis temperature is higher than 145 °C as there will be more time for synthesis while it is heating up. However, when analysed by the SEM only residue could be seen. It wasn't until a further 20 minutes had gone by in S33C that there were the first signs of NW's but strangely, no NP's.

Once three reasonable sized samples have been taken, there is not a lot of the mix left to continue to the end of a normal length synthesis. It's quite a tricky process to extract a sample during synthesis because you almost need three hands. The force required to insert the syringe through the septum is considerable, so you are required to support the equipment with one hand using paper as an insulator or a thermal glove whilst pushing the syringe through with the other. Once it's through the septum, two hands are required to draw the sample, one to hold the main body of the syringe and the other to draw the plunger. Once the sample has been taken the equipment requires support again while the syringe is being withdrawn. Care must also be taken to ensure that the body of the syringe does not come away from the needle or it is possible for ambient air to get into the flask through the needle.

From Table 14 the average NW diameter is about 85 nm and aspect ratio 16. Considering that the first signs of and particles or wires was found in this sample, an aspect ratio of 16 is impressive. The previous sample, taken only 20 minutes earlier showed only residue. For this reason, it was also decided to wash the NP and NW's more than was done in the trial in an attempt to wash away more organics.

6.5.3 During Synthesis Sampling

6.5.3.1 Results

As only 3 needles were available, only 3 samples were taken during synthesis labelled A, B and C. The synthesis was abandoned after these samples were taken because the quantity was reduced so much. The abandoned synthesis could also be analysed as a sample labelled D. The equipment cleaned and restarted with the identical synthesis which could be analysed as normal. The synthesis that samples were taken from was synthesis 37 so the following complete synthesis was 38.

6.5.3.1.1 Synthesis 37A Results

From Table 15 and Table 16. At time equals zero, when the stirrer is normally stopped, both NP and NW's could be seen. The average NP diameter (194.4 nm) was greater than the average NW diameter (154.5 nm).

It was expected that these particles would start small and grow over time prior to nanowires growing from them. It is also surprising that some nanowires are already starting to grow at the very beginning of the synthesis process. Although they only have an average aspect ratio of about 5, they are definitely not particles.

6.5.3.1.2 Synthesis 37B Results

From Table 17 and Table 18. It's interesting that there appears to be two different lengths of NW's. The long ones (50.8 nm) being over 6 times the short lengths (8.3 nm). Again, the NP average diameters are smaller than both the average NW diameters.

6.5.3.1.3 Synthesis 37C Results

From Table 19. It is noticed that the NP diameters have remained the same as with sample 37B an hour earlier at around 120 nm. However, the average NW diameter appears to have become smaller (from 169 to 152). Probably close enough to be differences in local size samples.

6.5.3.1.4 Synthesis 37D Results

From Table 20 and Table 21. This time the average NP diameters are larger than the average NW diameters. This might be the influence of a few very large NP's in the image amongst many more similar sized ones. These four samples are analysed together in the following section.

6.5.3.1.5 During Synthesis Sampling Summary

Table 22 tabulates the results of the samples taken. Samples A and D are larger NP's than B and C.

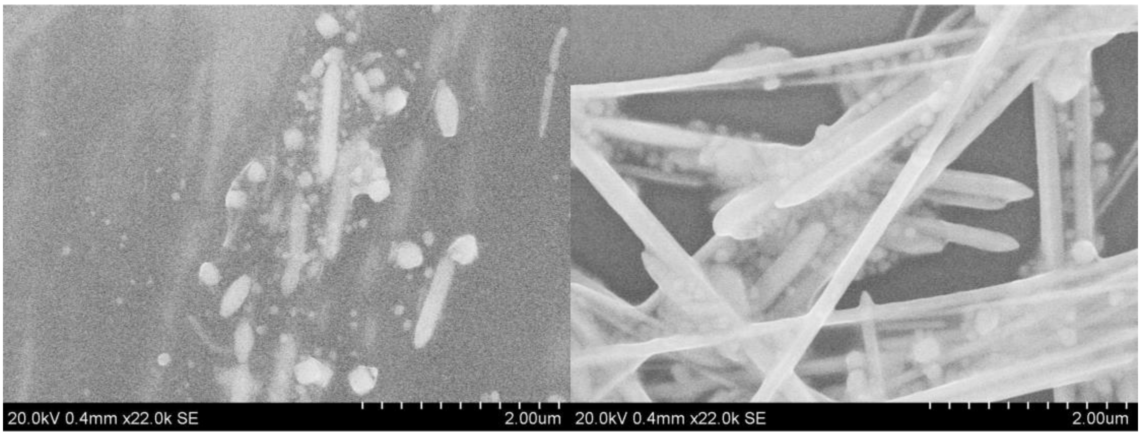


Figure 42 Synthesis 37A-02 and 37D-02 Micrographs

Looking at Figure 42 above, it's quite interesting to see the beginning of NP and NW growth. However, in both the micrographs analysed from 37A-02 and 37D-02, there are very much two sizes of NP's. It's possible that the larger ones are of different composition to the smaller ones. Obviously, the larger ones raise the average in both 37A and 37D. Obviously, the NP's are not shrinking and growing again between samples so it can only be a local difference.

The NW diameters appear to have remained roughly the same throughout the sampling times whereas the lengths have increased as expected. This meant that the aspect ratio increased from around 5 to 175 during the sampling time of 150 minutes and only managed 260 after 17 hours. So the aspect ratio is increasing at over 1 NW diameter per minute. If this rate continues, then the synthesis process would take less than 5 hours.

The diameter of the NW's doesn't change much during the synthesis process as they are all much the same and the last sample taken is actually the smallest of all. However, in S38 when the synthesis was run without interruption, the diameter seems significantly smaller. It doesn't seem likely that the NW's change diameter during synthesis so it so unless the synthesis quantity makes a difference, it is either local differences or slight differences between the mix.

The purity of our oleylamine is only 70% so there may be slight differences between syntheses because of the 30% contaminates. It is possibly worth shaking the bottle for a while prior to measuring out in an attempt to reduce any differences. If it isn't shaken then lighter contaminants may be at the top of the bottle but be reduced with each mix.

7 CONCLUSIONS

Although problems were encountered throughout this research, mostly beyond the control of the author, it has been a very stimulating, exciting and successful research project. As aims 1 and 2 are inextricably linked, they cannot completely be separated in these conclusions.

7.1 First Aim

The first aim (Increase aspect ratio of NW's >=400.) was to improve the aspect ratio and was achieved in the first two weeks at 190-195 °C synthesis temperature. Synthesis number 5 had an aspect ratio of 788 and a nickel content of 8.9% with 0.2 g glucose. The research went on with trials to lower the synthesis temperature while varying the glucose content to see what effects temperature has on the aspect ratio and nickel content. The first aim was achieved at each temperature down to 125 °C. It was also found that the aspect ratio increased as the synthesis temperature was lowered. The maximum aspect ratio found was 974 at a synthesis temperature of 155 °C in synthesis number 31 with 0.6 g glucose. However, in the time available it was not possible to increase the nickel content sufficiently to meet the second aim. When examining the overall data, the nickel content is expected to be in the correct range (5-20%) when between 1.0 to 1.5 g of glucose is added for a synthesis temperature of 155 °C.

7.2 Second Aim

The second aim (Control Ni content of CuNi alloy NW (between 5% - 20% Ni).) so as to reduce oxidation of the nanowires over time. Again, this was achieved in the first two weeks (synthesis 5) and many times again throughout the research down to 160 °C. Synthesis number 39 had an aspect ratio of 522 and a nickel content of 15.3% with 1 g glucose. Synthesis 39 was used to vary the ink concentration and thickness to find the best combination to optimise the third aim. Synthesis 28 with an aspect ratio of 456 and Ni content of 9.2% when 0.75 g glucose was added at a synthesis temperature of 165 °C was used as a comparison for the third aim.

7.3 Third Aim

Syntheses 28 and 39 were used for aim 3a (Optimise the optoelectronic properties (resistivity / transparency).). Concentrations of ink between 10 mg/ml, 20 mg/ml, 30 mg/ml and 40 mg/ml were made from synthesis 39 and applied using the 3 Mayer rods #4, #8 and #12. While concentrations of 20 mg/ml and 40 mg/ml were made from syntheses 28. #12 Mayer rod was used for these samples with the addition of #8 for the 40 mg/ml synthesis 28. Table 26 on page 91 is a summary of these results. Synthesis 28 with 20 mg/ml concentration ink, spread with #12 Mayer rod had a transmission of 80% of blank glass ranged from 10-20 Ω/□ sheet resistance was a good result. As was synthesis 39 with 30 mg/ml concentration ink spread with #12 Mayer rod and a transmission of 85% of glass and 59 Ω/□ sheet resistance. But the best combination found was synthesis 39 with 40 mg/ml concentration ink spread with #4 Mayer rod also had a transmission of 85% that of glass but only an average sheet resistance of 25 Ω/□. This is quite close to expected results from ITO and is good enough to be used as an alternative.

Aim 3b (Study and record oxidation resistance and transmission of coated substrates throughout the project.) was to test an early synthesis that met aims 1 and 2 throughout the project. Synthesis 5 was used for this purpose throughout the project and syntheses 28 and 39 at the end. Although the optoelectronic properties of syntheses 28 and 39 were very good they could only be resistance tested for a maximum of 2 weeks. Although these samples were kept in a 50 °C oven to accelerate the oxidation properties with little if any increase in resistance, the time is considered too short to predict long term oxidation resistance. However, although synthesis 5 with 40 mg/ml and spread with #12 Mayer rod was too dark for optimum transmission, only allowing 70% of the light through plain glass, the resistance ranged between 2 and 7 Ω/□. What is more, there was a total of 112 days of which 50, the sample were kept in the 50 °C oven and the last measurement was identical to the first with only small variations in between. These results give confidence that 8.9% nickel content inhibits oxidation of the CuNi alloy nanowires.

7.4 Fourth Aim

The fourth aim, (To better understand how anisotropic growth works. (Personal Aim)) was tackled by During Synthesis Sampling in section 5.5 which yielded very interesting results. The initial lack of NP's was a surprise and more experiments in this area would be required to fully fulfil this aim. It may be possible to complete a synthesis in one day rather than over two but a little more work is necessary to prove it. Table 22 Growth During Synthesis Summary on page 81 summarised these results. In many micrographs taken using the SEM, two different length NW's were present in different areas of the same view. The synthesis appeared to happen inside bubble like structures that grew over time. One explanation for the difference in lengths might be that earlier sampling, broke some of these bubbles that remained in the mix. Once a bubble is burst, growth stops. This is why the smaller wires appeared similar to previous samples taken.

This is a very interesting area of this research but the author was unable to find any other research where samples were taken during synthesis.

7.5 General Conclusions

It has been discovered that when more glucose is added to syntheses, more Ni is incorporated into the NW's as a CuNi alloy. As the synthesis temperature is lowered, more glucose is necessary to achieve the same Ni content in the wires. As the synthesis temperature is lowered, the aspect ratio increases but the Ni content is reduced so a compromise is necessary to balance the aspect ratio with oxidation resistance. It was found that with a Ni content of 8.9%, the sample did not oxidise over 112 days when 50 of these were in a 50 °C oven to accelerate the process. The last sheet resistance measurement was the same as the first.

The main target of this research was to synthesise copper-nickel alloy nanowires that are transparent and conductive enough to replace Indium Tin Oxide. This has been achieved and no special coatings are necessary to protect the NW's as they are inherently oxidation resistant.

8 FUTURE RESEARCH

As mentioned, the main focus for taking forward this research, should be for fine tuning the processes to establish the most effective method to produce high aspect ratios, perfect nickel content and the most efficient processes for production.

8.1 Improving Processes

Continue during syntheses sampling at, 3, 4, 5 and 6 hours for the same mix to see if a synthesis can be done daily. These four samples could be done in one day, still leaving time to repeat the same mix overnight conventionally for comparison. If the full aspect ratio is reached within 6 hours, then two syntheses a day could be achieved.

Spend time to find out why the UV curing method didn't work. This will also save so much time throughout the project and make the process suitable for R2R.

8.2 Improving Methods

Prepare syntheses at 190 °C between 0.12 and 2.4 g glucose in 0.04 steps so as to get a 4 point curve and optimise for Ni content and aspect ratio.

Spend time to find level of glucose for each temperature to find optimum Ni content at each temp. Especially 155 °C at about 1.25 g glucose. If that works go to 150 °C with higher glucose etc.

Once optimum mix for each temperature is known, spend more time finding best ink concentrations for each along with best Mayer rod for each to give best optoelectronic performance.

Next year Cranfield will install two more SEM's so it should be easier and quicker to find aspect ratios and Ni contents. Book plenty of sessions early so as to be able to regularly characterise syntheses done to date and be better informed to choose the next syntheses.

REFERENCES

1. Kang M-G., Kim M-S., Kim J., Guo LJ. Organic Solar Cells Using Nanoimprinted Transparent Metal Electrodes. Advanced Materials. 2008; 20(23): 4408–4413. Available at: DOI:10.1002/adma.200800750

2. Forget S., Chenais S., Siove A. Organic Light-Emitting Diodes. Photochemistry and Photophysics of Polymer Materials. 2010; 4(1): 309–350. Available at: DOI:10.1002/9780470594179.ch9

3. Rathmell AR., Bergin SM., Hua YL., Li ZY., Wiley BJ. The growth mechanism of copper nanowires and their properties in flexible, transparent conducting films. Advanced Materials. 2010; 22(32): 3558–3563. Available at: DOI:10.1002/adma.201000775

4. Deng B., Hsu PC., Chen G., Chandrashekar BN., Liao L., Ayitimuda Z., et al. Roll-to-Roll Encapsulation of Metal Nanowires between Graphene and Plastic Substrate for High-Performance Flexible Transparent Electrodes. Nano Letters. 2015; 15(6): 4206–4213. Available at: DOI:10.1021/acs.nanolett.5b01531

5. Wuttig M., Yamada N., Lankhorst MH., Ketelaars BW., Wolters R a., Raoux S., et al. The minimum energy per bit obtained with our sharpest (~20 ns) pulses is of the order ~100 fJ. However, the linear trend of V. Science. 2011; (April): 4–7.

6. Singh R., Tharion J., Murugan S., Kumar A. ITO-Free Solution-Processed Flexible Electrochromic Devices Based on PEDOT:PSS as Transparent Conducting Electrode. ACS Applied Materials and Interfaces. 2017; 9(23): 19427–19435. Available at: DOI:10.1021/acsami.6b09476

7. Kim N., Kee S., Lee SH., Lee BH., Kahng YH., Jo YR., et al. Highly conductive PEDOT:PSS nanofibrils induced by solution-processed crystallization. Advanced Materials. 2014; 26(14): 2268–2272. Available at: DOI:10.1002/adma.201304611

8. De S., Higgins TM., Lyons PE., Doherty EM., Nirmalraj PN., Blau WJ., et

al. Silver Nanowire Networks as Flexible ,. 2009; 3(7): 1767–1774.

9. Rathmell AR., Wiley BJ. The synthesis and coating of long, thin copper nanowires to make flexible, transparent conducting films on plastic substrates. Advanced Materials. 2011; 23(41): 4798–4803. Available at: DOI:10.1002/adma.201102284

10. Chen T-H., Chen T-Y. Effects of Annealing Temperature on Properties of Ti-Ga–Doped ZnO Films Deposited on Flexible Substrates. Nanomaterials. 2015; 5(4): 1831–1839. Available at: DOI:10.3390/nano5041831

11. Arnold MS., Stupp SI., Hersam MC. Enrichment of single-walled carbon nanotubes by diameter in density gradients. Nano Letters. 2005; 5(4): 713–718. Available at: DOI:10.1021/nl050133o

12. Eom H., Lee J., Pichitpajongkit A., Amjadi M., Jeong JH., Lee E., et al. Ag@Ni core-shell nanowire network for robust transparent electrodes against oxidation and sulfurization. Small. 2014; 10(20): 4171–4181. Available at: DOI:10.1002/smll.201400992

13. Xu C., Wang Y., Chen H., Zhou R., Liu Y. Large-scale synthesis of ultralong copper nanowires via a facile ethylenediamine-mediated process. Journal of Materials Science: Materials in Electronics. 2014; 25(5): 2344–2347. Available at: DOI:10.1007/s10854-014-1882-6

14. Ye S., Rathmell AR., Stewart IE., Ha Y-C., Wilson AR., Chen Z., et al. A rapid synthesis of high aspect ratio copper nanowires for high-performance transparent conducting films. Chem. Commun. 2014; 50(20): 2562–2564. Available at: DOI:10.1039/C3CC48561G

15. Han S., Hong S., Ham J., Yeo J., Lee J., Kang B., et al. Fast plasmonic laser nanowelding for a Cu-nanowire percolation network for flexible transparent conductors and stretchable electronics. Advanced Materials. 2014; 26(33): 5808–5814. Available at: DOI:10.1002/adma.201400474

16. Yin Z., Lee C., Cho S., Yoo J., Piao Y., Kim YS. Facile synthesis of oxidation-resistant copper nanowires toward solution-processable, flexible,

foldable, and free-standing electrodes. Small. 2014; 10(24): 5047–5052. Available at: DOI:10.1002/smll.201401276

17. Nam V., Lee D. Copper Nanowires and Their Applications for Flexible, Transparent Conducting Films: A Review. Nanomaterials. 2016; 6(3): 47. Available at: DOI:10.3390/nano6030047

18. Li S., Chen Y., Huang L., Pan D. Large-Scale Synthesis of Well-Dispersed Copper Nanowires in an Electric Pressure Cooker and Their Application in Transparent and Conductive Networks. 2014; Available at: DOI:10.1021/ic500094b

19. Lee D., Paeng D., Park HK., Grigoropoulos CP. Vacuum-free, maskless patterning of Ni electrodes by laser reductive sintering of Nio nanoparticle ink and its application to transparent conductors. ACS Nano. 2014; 8(10): 9807–9814. Available at: DOI:10.1021/nn503383z

20. Matei E., Enculescu I., Toimil-Molares ME., Leca A., Ghica C., Kuncser V. Magnetic configurations of Ni-Cu alloy nanowires obtained by the template method. Journal of Nanoparticle Research. 2013; 15(8). Available at: DOI:10.1007/s11051-013-1863-3

21. Rathmell AR., Nguyen M., Chi M., Wiley BJ. Synthesis of oxidation-resistant cupronickel nanowires for transparent conducting nanowire networks. Nano Letters. 2012; 12(6): 3193–3199. Available at: DOI:10.1021/nl301168r

22. Shanlene M., Delavega DC., Donnabelle M., Balela L. Synthesis of Copper-Nickel Nanowires by Two-Step Method. 2015; 6: 1–4.

23. Stewart IE., Rathmell AR., Yan L., Ye S., Flowers PF., You W., et al. Solution-processed copper–nickel nanowire anodes for organic solar cells. Nanoscale. 2014; 6(11): 5980. Available at: DOI:10.1039/c4nr01024h

24. Song J., Li J., Xu J., Zeng H. Superstable transparent conductive Cu@Cu4Ni nanowire elastomer composites against oxidation, bending, stretching, and twisting for flexible and stretchable optoelectronics. Nano

Letters. 2014; 14(11): 6298–6305. Available at: DOI:10.1021/nl502647k

25. Udayabhaskar R., Ollakkan MS., Karthikeyan B. Preparation, optical and non-linear optical power limiting properties of Cu, CuNi nanowires. Applied Physics Letters. 2014; 104(1). Available at: DOI:10.1063/1.4858406

26. Xue J., Song J., Zou Y., Huo C., Dong Y., Xu L., et al. Nickel concentration-dependent opto-electrical performances and stability of Cu@CuNi nanowire transparent conductors. RSC Adv. Royal Society of Chemistry; 2016; 6(94): 91394–91400. Available at: DOI:10.1039/C6RA19577F

27. Lonne, Q. Kamau, JM. Endrino, J. Huang Z. Copper-Nickel nanowires for transparent conductive electrodes. European Conference on Nanofilms, ECNF2016. Bilbao, Spain, 19-21 October 2016.: Presentation at Conference.; 2016.

28. Mourdikoudis S., Liz-marza LM. Oleylamine in Nanoparticle Synthesis. 2013; Available at: DOI:10.1021/cm4000476

29. Tokuno T., Nogi M., Karakawa M., Jiu J., Nge TT., Aso Y., et al. Fabrication of silver nanowire transparent electrodes at room temperature. Nano Research. 2011; 4(12): 1215–1222. Available at: DOI:10.1007/s12274-011-0172-3

30. Gaynor W., Burkhard GF., McGehee MD., Peumans P. Smooth nanowire/polymer composite transparent electrodes. Advanced Materials. 2011; 23(26): 2905–2910. Available at: DOI:10.1002/adma.201100566

31. De S., J.King P., E.Lyons P., Khan U., N.Coleman J. Size Effects and the problem with percolation in nanostructures transparent conductors. ACS Nano. 2010; 4(12): 7064–7072.

32. E.G.West. Copper and its alloys. Ellis Horwood Limited; 1982. 241 p.

33. Association C development. Copper and copper alloy data: Data Sheets K1, K2, K3. Potters Bar; 1972.

34. Lonne Q., Endrino J., Huang Z. UV Treatment of Flexible Copper Nanowire

Mesh Films for Transparent Conductor Applications. Nanoscale Research Letters. Nanoscale Research Letters; 2017; 12. Available at: DOI:10.1186/s11671-017-2343-y

35. Lee, J.Y. Connor, S.T. Cui, J.J. Peumans, P. Solution-processed metal nanowire mesh transparent electrodes. Nano Letters 2008, 8, 689-692.

36. Askari, H., Fallah, F., Askari, M., Mohmmadieyh, MC. Electrical and Optical Properties of ITO thin films prepared by DC magnetron sputtering for low-emitting coatings. Isfahan University, Iran.

37. Gordon RG. Preparation and Properties of Transparent Conductors. Materials Research Society Symp. Proc. Vol 426 1996 pg420.

38. Ossila. Sheet Resistance: A Guide to Theory. https:/www.ossila.com/pages/sheet-resistance-theory 2018.

APPENDICES

Appendix A Original SOP

SOP FOR THE FABRICATION OF CuNi NW TCEs

SYNTHESIS

Put 0.4092 g (2.4 mmol) of copper II chloride dihydrate ($CuCl_2.2H_2O$) in a round bottom flask.

Add 0.2986 g (1.2 mmol) of nickel II acetate tetrahydrate ($Ni(C_2H_3O_2)_2.4H_2O$) in the round bottom flask.

Add 0.25-1.00 g (1.4-5.6 mmol) of glucose ($C_6H_{12}O_6$) in the round bottom flask.

Add 25 mL of oleylamine ($C_{18}H_{37}N$) in the round bottom flask.

Add a magnetic stirrer in the round bottom flask.

Put the round bottom flask in an oil bath (on a magnetic stirring hotplate) and connect the round bottom flask to a reflux column. Connect a bubbler on top of the reflux column (for N_2 flow).

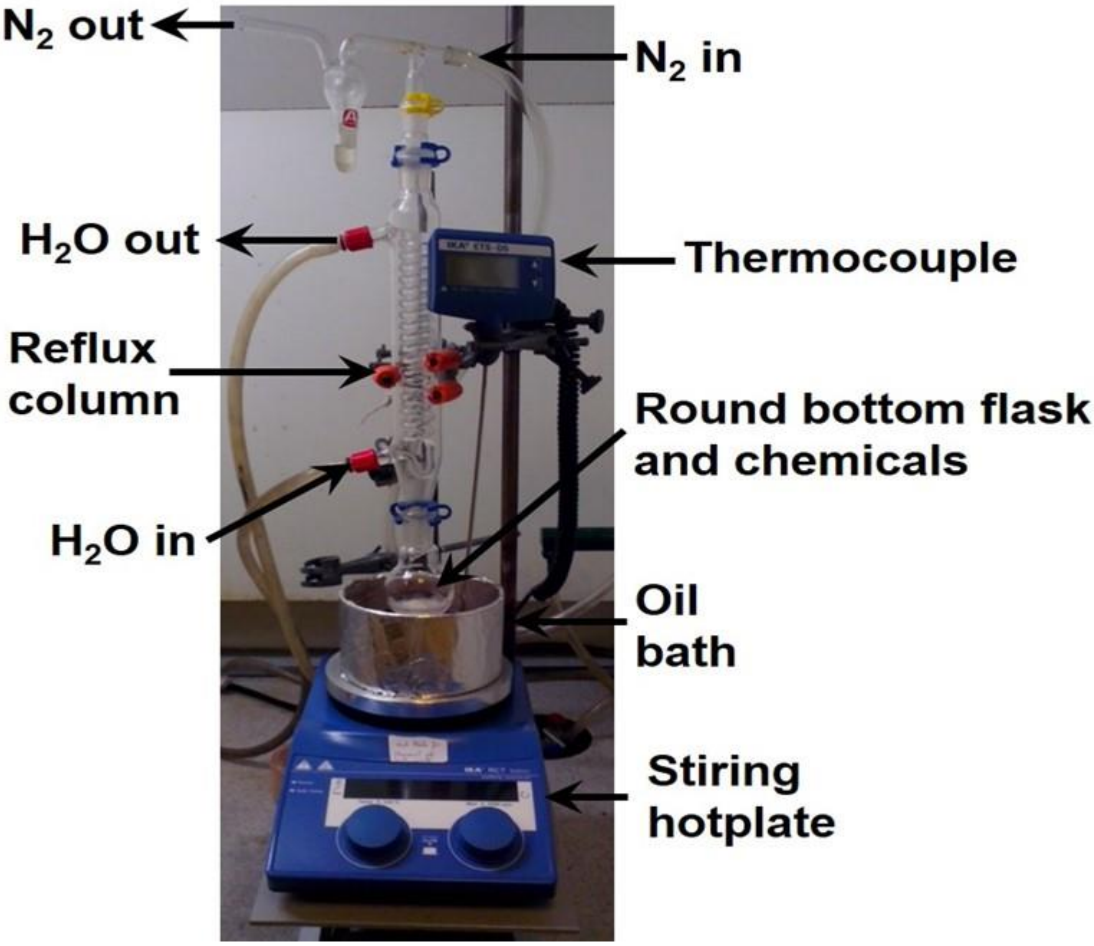
Start the water flow for the reflux column and the N_2 flow.

Heat the solution at 95 °C for 30 min with a 800-rpm stirring to remove $O_2(g)$ and water traces. At that stage the solution is blue.

Heat the solution at 195 °C for 30-60 min with a 800-rpm stirring to reduce Cu and Ni and form CuNi seeds. The colour of the solution will progressively become dark brown to black depending on the Ni content in the CuNi alloy.

Stop the stirring and keep the solution at 195 °C for 16 hrs to make the CuNi NWs grow.

Stop the heating and let the solution cool down naturally.



Set-up for the synthesis of the CuNi NWs

WASHING

Transfer the solution in a 50-mL flask adapted to centrifuge and add hexane in the flask (total volume ≈ 40 mL).

Vortex the solution in manual mode for 2 minutes, then centrifuge at 4000 rpm for 20 minutes (tilt on position 3 on the centrifuge).

Remove the supernatant from the flask with a pipette.

Repeat the vortex / centrifuge process at least:

- 2 times with hexane
- 2 times with isopropyl alcohol (IPA)
- 1 time with acetic acid

- 3 times with IPA

If necessary, repeat the vortex / centrifuge process 1 more time with acetic acid and 3 times with IPA. With acetic acid and IPA, 2-5 minutes of centrifuge can be enough.

At the end, store the Cu NWs in a 20-mL flask with about 10 mL of IPA

Vortexer

Centrifuge

INK

Mix 10 mL of IPA containing 0.5 wt% of polyvinylpyrrolidone (PVP, 10,000 g.mol^{-1}) and 3 mL of ethyl acetate.

Evaporate all the IPA contained in the 20-mL flask with the CuNi NWs

Add the CuNi 0.5wt%PVP-IPA/ethyl acetate mix in the flask with the CuNi NWs to obtain the desired concentration (ca. 10-40 mg/mL).

Vortex the CuNi NWs ink at 10 Hz in automatic mode for 0.5-3 hours to disperse the Cu NWs in the ink. Some parafilm has to be wrapped around the bottom of the 20-mL flak to ensure a good friction with the flask holder and a good support during the vortex.

COATING

To coat a substrate, use a micro-pipette to form a straight line of ink parallel to the upper edge of the substrate.

Then quickly spread the ink with a Mayer rod, sliding (not rolling) the rod down towards yourself, without applying to much pressure.

Let the solvents evaporate.

For a substrate of ca. of 10x10 cm (in general, PET), use 100-200 µL of ink.

For a substrate of ca. 1.5x7.5 cm (in general, a microscope glass slide cut to size), 20-30 µL of ink are enough.

The rods #4, #8 and #12 from Dyne Testing have wire diameters of ca. 0.1, 0.2 and 0.3 mm and form wet films of ca. 10.2, 20.3 and 30.5 µm).

POST TREATMENTS

Perform a thermal treatment at 350 °C, for 3 hrs, under 5%H2-95%Ar or under pure N_2.

This is only possible with glass substrates, not PET (T_f = 245 °C).

Polyimide PI (T_f = 400 °C) has also been tested as a flexible substrate and seems to withstand very well that kind of thermal treatment but PI has poor transparency.

A UV treatment of 2 or 4 min in ambient conditions, followed by an acid bath of 10 min at room temperature has given good results on pure Cu NWs. It has not been tried on CuNi NWs.

Appendix B Original CPA Expansion of Processes

Figure 43 Original CPA Expansion 1

Figure 44 Original CPA Expansion 2

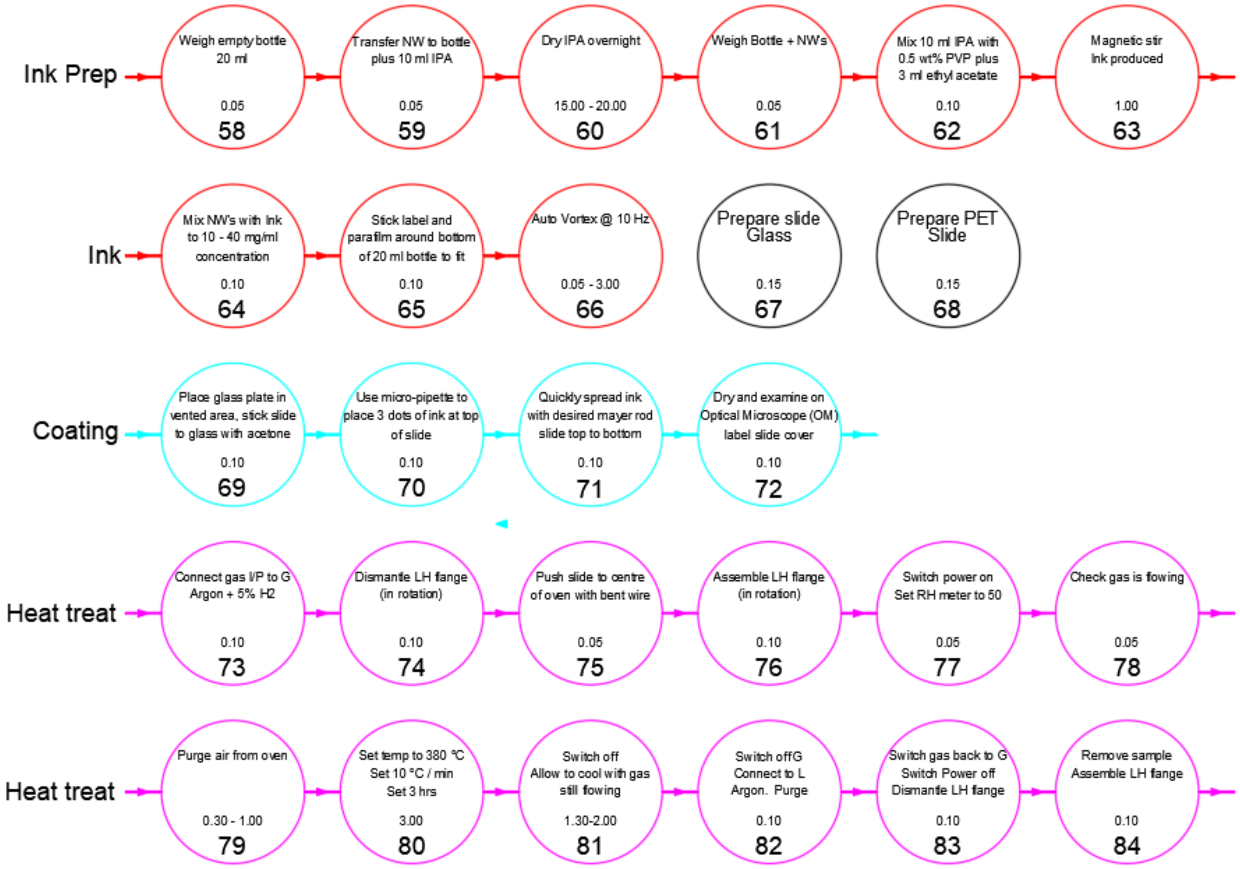


Figure 45 Original CPA Expansion 3

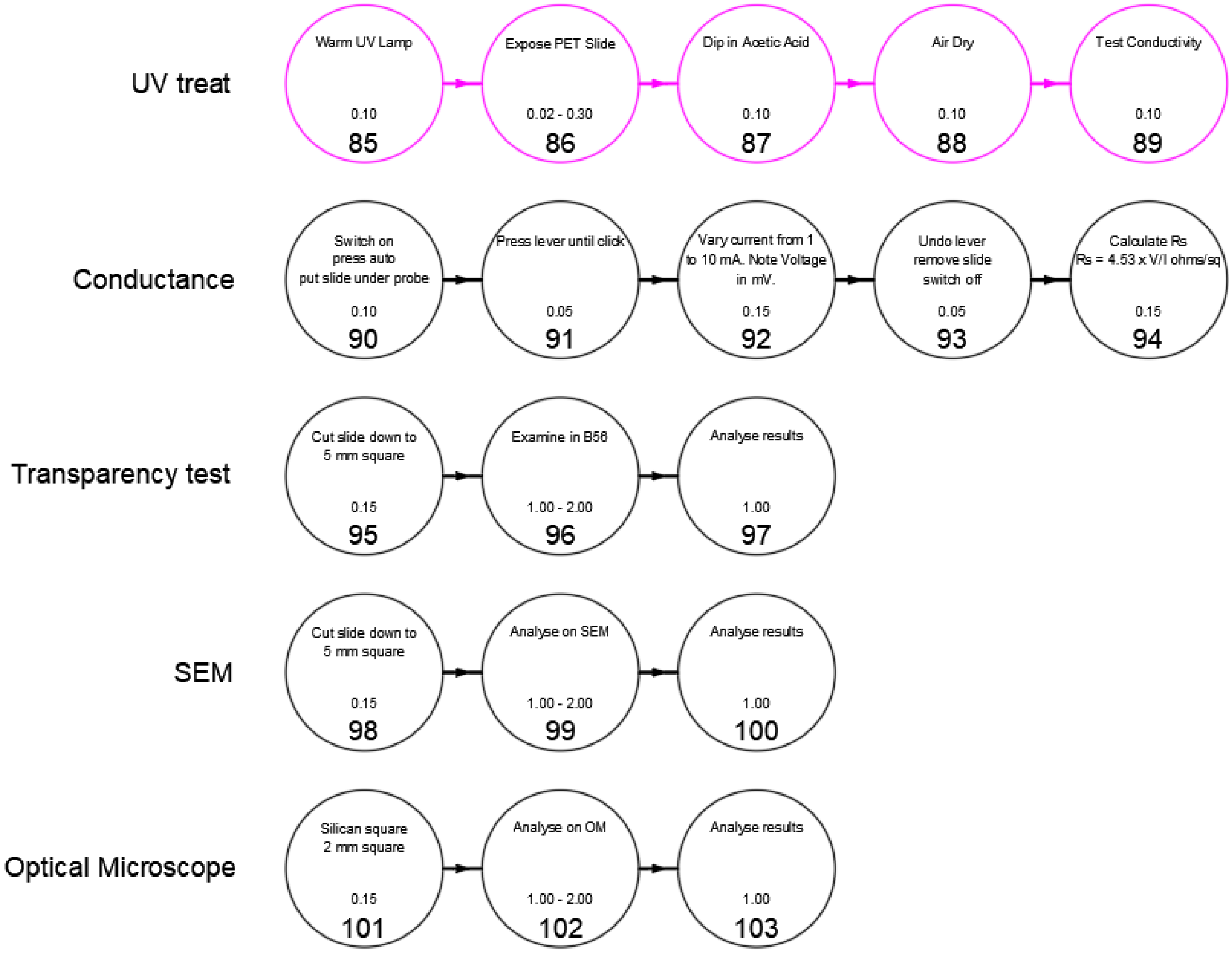


Figure 46 Original CPA Expansion 4

Appendix C Revised CPA Outline

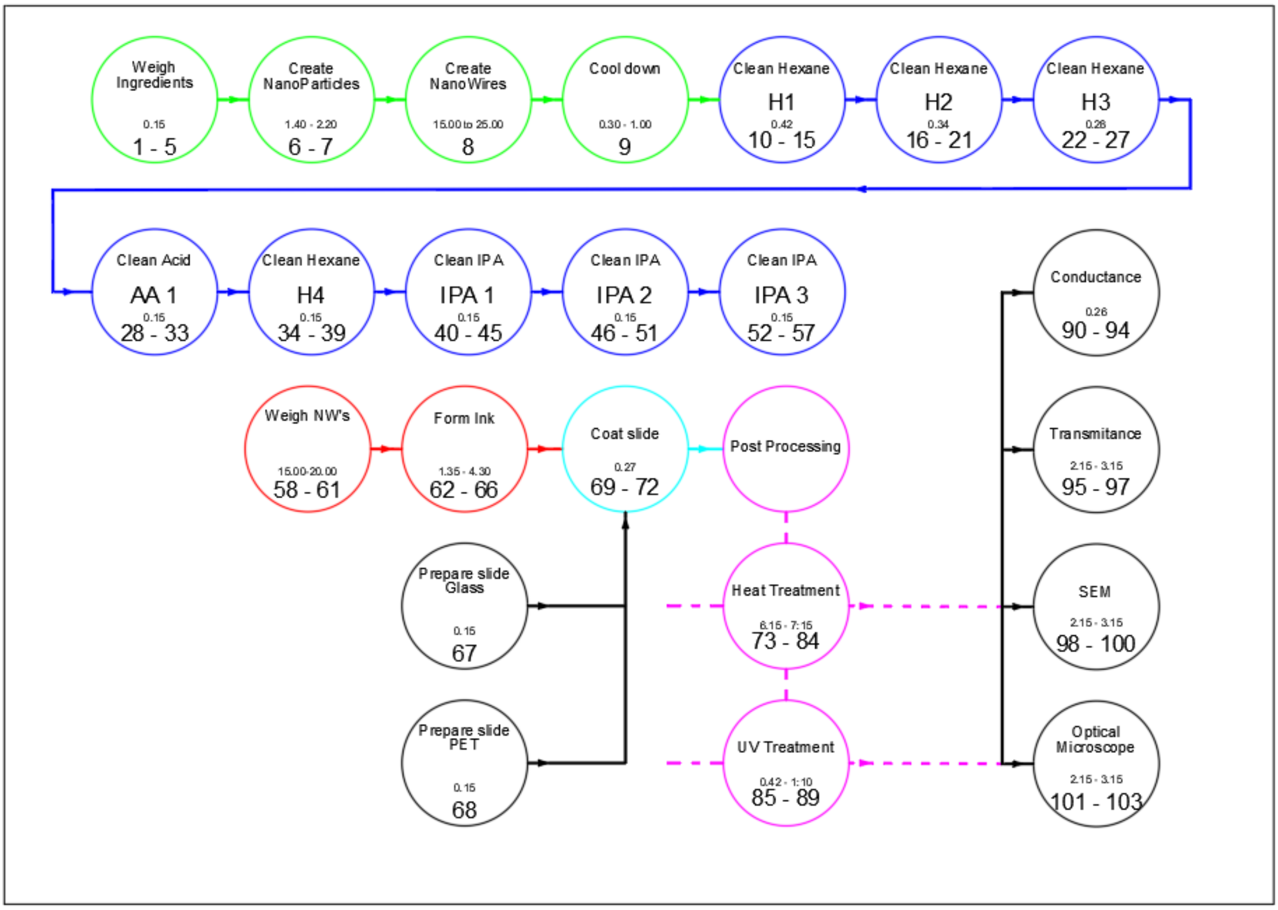


Figure 47 Revised CPA

Appendix D Revised CPA Expansion of Processes

Figure 48 Revised CPA Expansion 1

Figure 49 Revised CPA Expansion 2

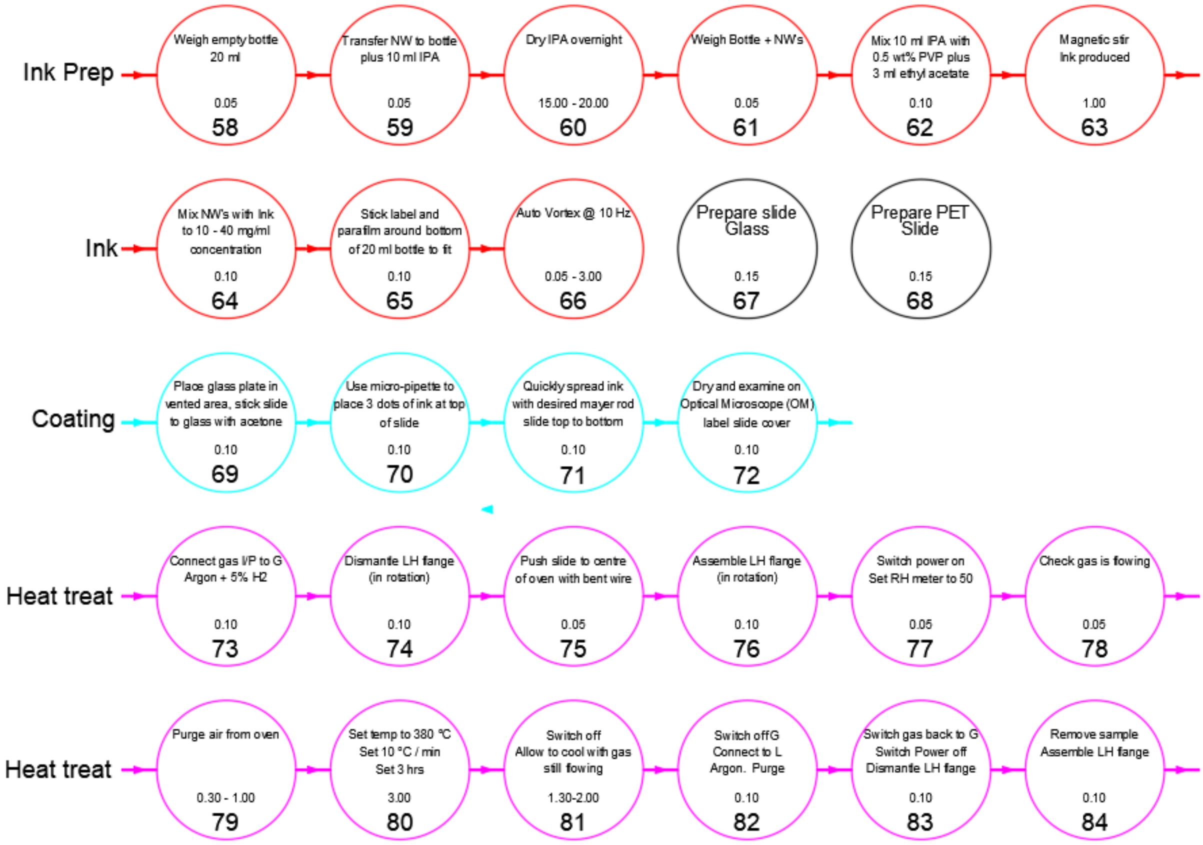


Figure 50 Revised CPA Expansion 3

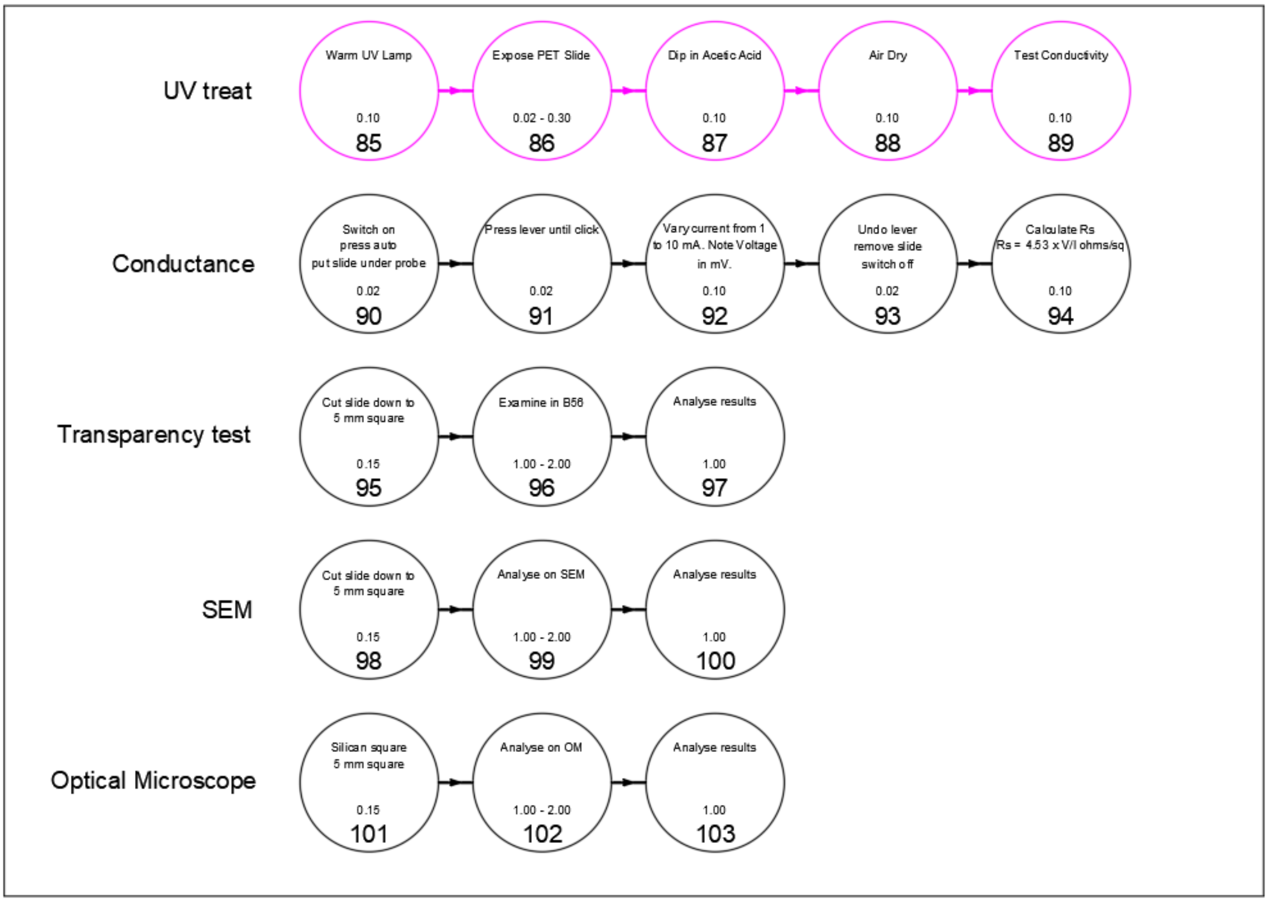


Figure 51 Revised CPA Expansion 4

Appendix E Revised SOP

SOP FOR THE FABRICATION OF CuNi NW TCEs PK

SYNTHESIS

Put 0.4092 g (2.4 mmol) of copper II chloride dihydrate ($CuCl_2.2H_2O$) in a round bottom flask.

> *Use small piece of paper with fold down middle; reset scales. Clean spatula. Put weighed material in 50 cl glass bowl (clean) in cork holder.*

Add 0.3285 g (1.3 mmol) of nickel II acetate tetrahydrate ($Ni(C_2H_3O_2)_2.4H_2O$) in the round bottom flask.

> *Clean spatula between compounds.*

Add 0.25-1.00 g (1.4-5.6 mmol) of glucose ($C_6H_{12}O_6$) in the round bottom flask.

> *Cleaning done with acetone, at least 3 times.*

Add 25 mL of oleylamine ($C_{18}H_{37}N$) in the round bottom flask.

> *Measure oleylamine inside hood using 25 cl measure tube.*

Add a magnetic stirrer in the round bottom flask.

Put the round bottom flask in an oil bath (on a magnetic stirring hotplate) and connect the round bottom flask to a reflux column. Connect a bubbler on top of the reflux column (for N_2 flow).

Make sure oil is above chemical level for even heating and that bottom of thermometer is as close to flask as possible and slightly lower than the bottom of the flask.

Start the water flow for the reflux column and the N_2 flow.

Heat the solution at 95 °C (LH dial) for 30 min with 800-rpm (RH dial) stirring to remove O_2(g) and water traces. At that stage the solution is blue.

> *Set heat to 120 °C (hotplate) and thermometer to 95 °C (feedback). While heating, wash out all equipment used, using acetone then soap and water finishing with acetone again; dry in oven. Pour waste into oleylamine waste bottle and acetone into acetone waste bottle.*

Heat the solution at 195 °C for 30-60 min with 800-rpm (RH dial) stirring to reduce Cu and Ni and form CuNi seeds. The colour of the solution will progressively become dark brown to black depending on the Ni content in the CuNi alloy.

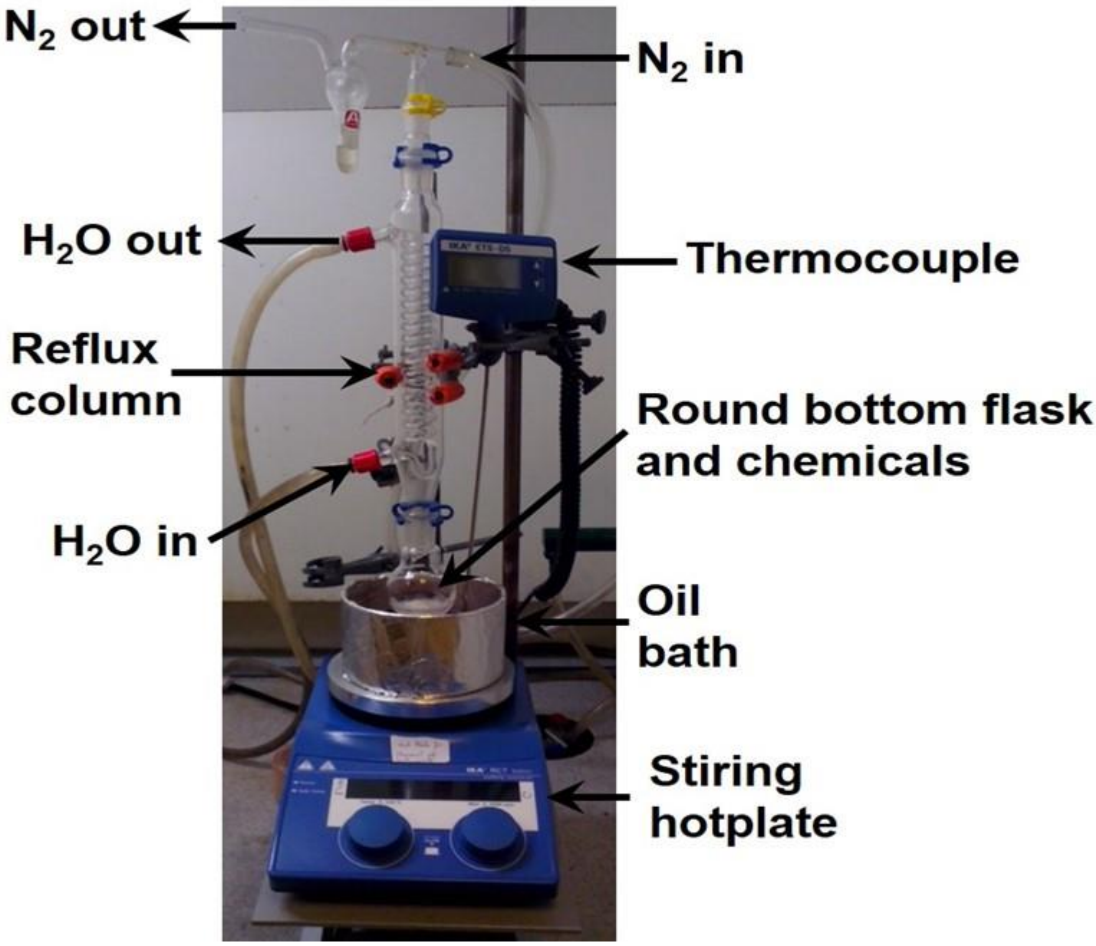
> *Set hotplate to 240 °C and thermostat to 195 °C. As the temperature rises slowly when it approaches the thermometer setting, set it high initially and turn down to required temperature when it approaches it otherwise the temperature takes forever to reach target.*

Stop the stirring and keep the solution at 195 °C for 16 hrs to make the CuNi NWs grow.

> *Overnight process, write form and leave near experiment. When glassware dry put back in drawer marked Quentin.*

Stop the heating and let the solution cool down naturally.

> *As oleylamine is so viscous, let cool down to 50-60 °C and fill bottle of Hexane and heat in drying oven to 50 °C ready for cleaning NW's.*



Set-up for the synthesis of the CuNi NWs

WASHING

Transfer the solution in a 50-mL flask adapted to centrifuge and add hexane in the flask (total volume ≈ 40 mL or just over).

> *Weigh bottle and contents and prepare a similar bottle full of water to the same weight to put opposite in the centrifuge so as to balance it.*

Vortex the solution in manual mode for 2 or 3 minutes, then centrifuge at 4000 rpm for 20-25 minutes (tilt on position 3 on the centrifuge).

Remove the supernatant from the flask with a pipette.

> *Do this very carefully so as not to mix the NW's with solution. Take solution out very carefully with pipette. Refill with Hexane and reweigh – prepare same weight water counterbalance.*

Repeat the vortex / centrifuge process at least:

- 2 more times with hexane
- 1 time with acetic acid *Don't leave in this as it eats NW's*
- 1 more time with hexane
- 3 times with IPA.

If necessary, repeat the vortex / centrifuge process 1 more time with acetic acid, 1 more with hexane and 3 times with IPA. With acetic acid and IPA, 2-5 minutes of centrifuge can be enough. The hexane after acetic acid only requires 2 minutes centrifuge.

At the end, store the Cu NWs in a 20-mL flask with about 10 mL of IPA

> *Before transferring to 20 ml bottle – weigh bottle and lid accurately. Label them both.*
>
> *We put a dot of NW solution on an optical slide which evaporated very quickly. We looked at the resultant NW's but the aspect ratio was very poor. Not possible to make accurate measurements with optical microscope. Started with the dot in one corner of the slide and will keep for comparison each time I make NW's. Also put a drop on silicon slice (7 mm x 5 mm) for SEM and EDS analysis.*

Vortexer

Centrifuge

INK

> *Weigh empty bottle and lid for NW's and label. Wash NW's into bottle with IPA and evaporate at room temperature so as not to conglomerate. Also, when it's pure Cu it will oxidise more when hot.*

Mix 10 mL of IPA containing 0.5 wt% of polyvinylpyrrolidone (PVP, 10,000 g.mol^{-1}) and 3 mL of ethyl acetate.

> *Mix 0.1 g PVP with 19.9 g IPA in small glass bottle and stir for 1 hour. In mean time evaporate all solution with NW's. Can decant solution from top once settled out.*

Evaporate all the IPA contained in the 10-mL flask with the CuNi NWs

Add the CuNi 0.5wt%PVP-IPA/ethyl acetate mix in the flask with the CuNi NWs to obtain the desired concentration (ca. 10-40 mg/mL).

Vortex the CuNi NWs ink at 10 Hz in automatic mode for 0.5-3 hours to disperse the Cu NWs in the ink. Some parafilm has to be wrapped around the bottom of the 20-mL flask to ensure a good friction with the flask holder and a good support during the vortex.

COATING

To coat a substrate, use a micro-pipette to form a straight line of ink parallel to the upper edge of the substrate.

> *Stick slide down to glass with suction (wringing) using acetone. Use about 30 µl (3x micro pipette).*

Then quickly spread the ink with a Mayer rod, sliding (not rolling) the rod down towards yourself, without applying to much pressure.

Let the solvents evaporate.

> *Examine slide on optical microscope for percolation and put in labelled container.*

For a substrate of ca. of 10x10 cm (in general, PET), use 100-200 µL of ink.

For a substrate of ca. 1.5x7.5 cm (in general, a microscope glass slide cut to size), 20-30 µL of ink are enough.

The rods #4, #8 and #12 from Dyne Testing have wire diameters of ca. 0.1, 0.2 and 0.3 mm and form wet films of ca. 10.2, 20.3 and 30.5 µm).

POST TREATMENTS

Thermal

Perform a thermal treatment at 350 °C, for 3 hrs, under 5%H2-95%Ar or under pure N_2.

This is only possible with glass substrates, not PET (T_f = 245 °C).

> *Dismantle LH flange and poke slide into centre of oven. Reassemble flange making sure that it is fitted parallel to the other flange. Check that the pipe connections go to the 5% H2 in argon valve (G). Set RH meter to about 50. Check that RH and LH valves are open. If required ask Tim to turn on gas bottle. Leave to purge all air from system for around 1 hour before turning temperature up to 380 °C for 3 hrs. Allow to cool to room temperature.*
>
> *To Set, press 1 (lh button), press 4 (rh button) until it reads 380*
>
> *Press 1 (SPrr), chose 10 °C/min with arrows (3 and 4)*
>
> *Press 1 (t1), use 3 and 4 to set 3 hrs*

Polyimide PI (T_f = 400 °C) has also been tested as a flexible substrate and seems to withstand very well that kind of thermal treatment but PI has poor transparency.

Once cooled down.

Switch G valve off. Unplug G valve with H_2 and N_2. Plug in L (Argon). Do not switch Argon line off!

Purge with Argon for 10 mins. Switch Argon off. Plug back into G without switching on. Switch power off. Unscrew flange, bit at a time and remove sample. Replace flange.

UV

A UV treatment of 2 or 4 min in ambient conditions, followed by an acid bath of 10 min at room temperature has given good results on pure Cu NWs. It has not been tried on CuNi NWs.

Warm bulb for 10 mins with cover over sample. Slide cover back using oven gloves (very hot!).

After each 2 mins test for conductivity until homed in on best time.

Try with one glass slide first.

Try with PET again. Once time understood, make PET slides for all 5 inks and redo.

MEASURING RESULTS

SEM

Book in for induction.

All samples have to have a thin conductive coating before viewing. Out CuNi NW's are normally sputter coated in a 10 nm gold layer prior to viewing them. To save time get them coated before you are booked to use the SEM. Use SEM efficiently as it costs between £30-50 / hour.

Our slides require cutting to size before coating and viewing, otherwise the gold coating will change their characteristics and make them useless for measuring transparency, conductivity or oxidation. I cut the end off where the drops of ink were applied and used that part for coating and viewing. This leaves the important centre part of the slide, with the most consistent and densest layer of NW ink for other tests.

SEM sample holder is either multiple of single. The multiple holder is not very secure so for high magnification work use the single holder. Place sample on single holder and screw down. Place back scatter plate in position if required. Close vacuum chamber and start vacuum pump down process. Wait until it just reaches 1.3 x 10^{-4} mBar, normally takes 3-4 mins. Best wait for 1.2 mBar.

Set aperture setting on vacuum chamber column. 6 – image, 5 – analyse.

Set spot size, accuracy and Voltage through software.

Set – Detectors – secondary electrons

Beam – 20 kV (between 5 – 20kV normally for imaging).

Set spot size – 5 for imaging, higher for higher mag.

If only 1 sample – set 0,0 on carousel. Change if multiple.

When vacuum reaches target, turn beam on (20 kV).

Focus first. Turn contrast down. RH mouse button to focus.

Increase mag by either, Pull down menu, + or – doubles or halves, big dial for fine adjustment.

To correct for stigmatism use mouse back and forward – OK – (db) displays correct working distance (WD).

WD needs to be <= 10 but change in stages.

Select an image that you want to capture at mag you want – set Focus/stig, contrast/brightness, mag/position.

Press F2 to slow scan the screen.

Software XL Docu.

EDX N2 filled column

Software – Aztec on LH computer

Set SEM – part and ID

10 nm coat click highlight from Left to Right

Set App 5, WD – 6

Mag – hr – EDX mode redo parameters#

Set image – bring to LH computer – start

Adjust contrast/brightness, acquire spectra

Atomic % and weight %

Area composition – about 2 um^2

CONDUCTANCE

Using the 4 point probe.

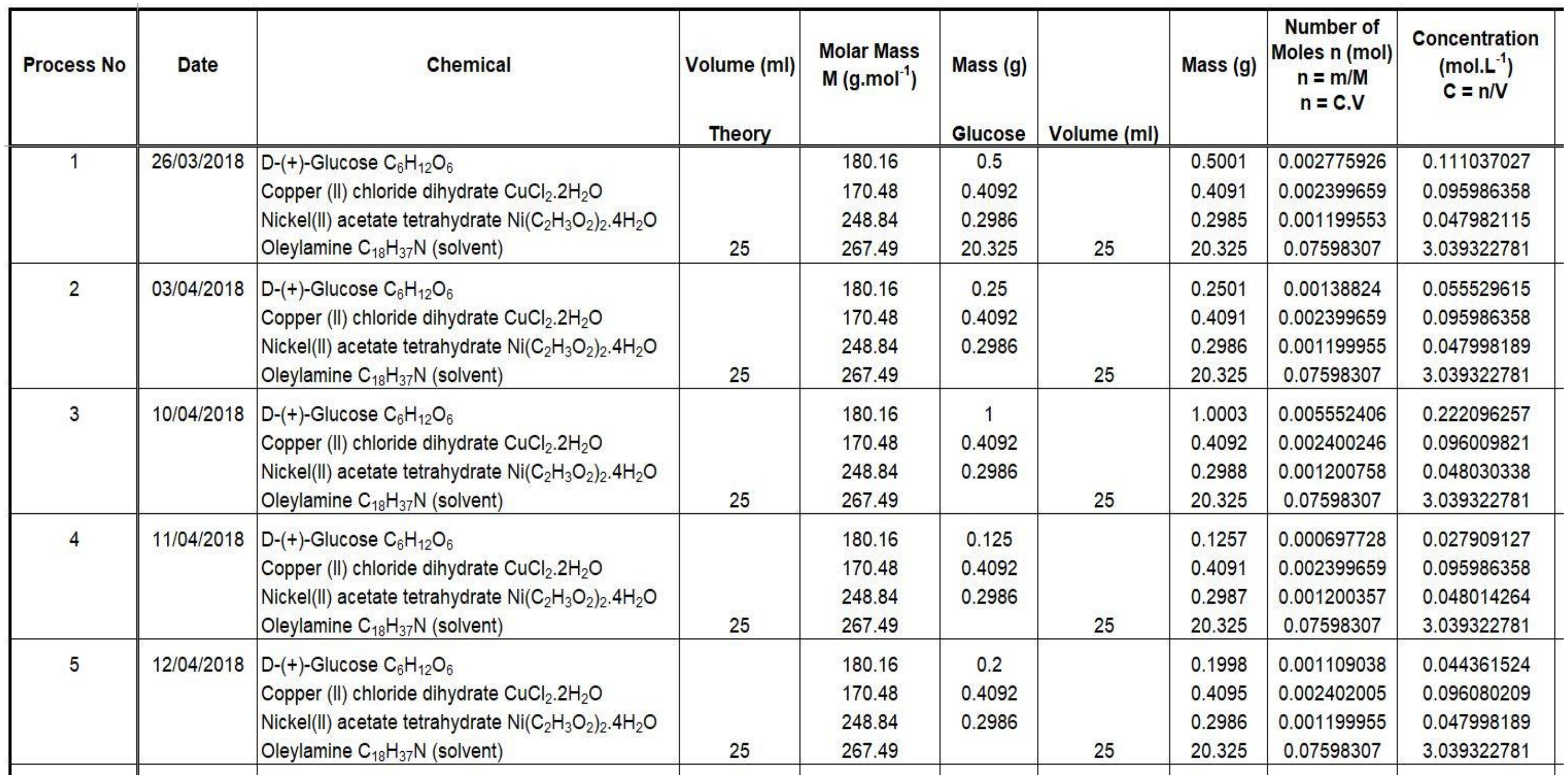
Switch on at wall with LH and 3rd switches. Switch red button on. Press auto. Put slide under probe. Press lever until it clicks. Vary current between 1 mA – 10 mA and note mV at each step. Work out Rs by formula, Rs = 4.53 x V / I

Results (synthesis 1)

Current (mA)	**Voltage (mV)**	**Rs (Ω/sq)**
1	20.25	91.7325
2	40.54	91.8231
3	60.83	91.8533
4	81.13	91.8797
5	101.45	91.9137
6	121.88	92.0194
7	142.27	92.0690
8	162.75	92.1572
9	183.27	92.2459
10	203.96	92.3939
Average		**92.0088**

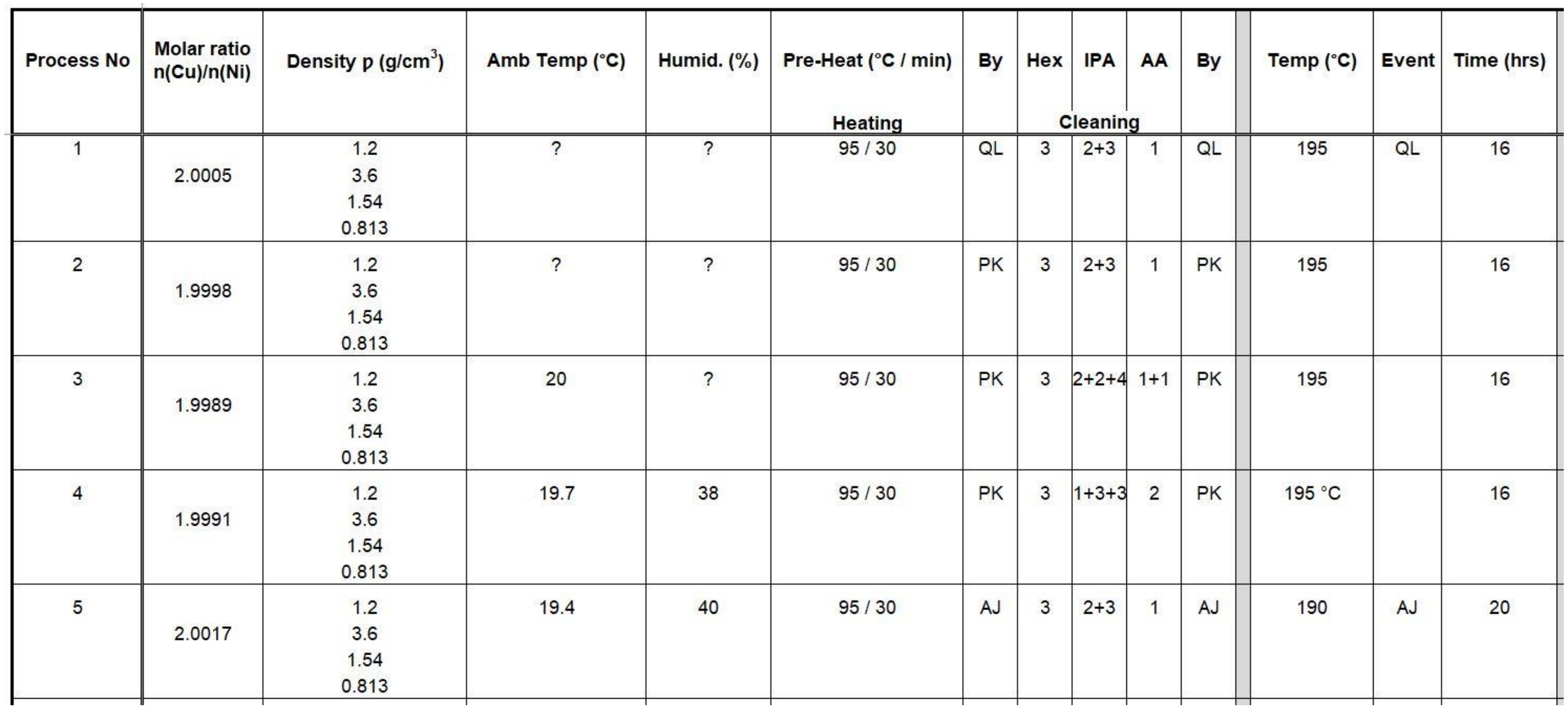
Undo lever. Remove slide. Switch off.

Appendix F Spreadsheet of Data



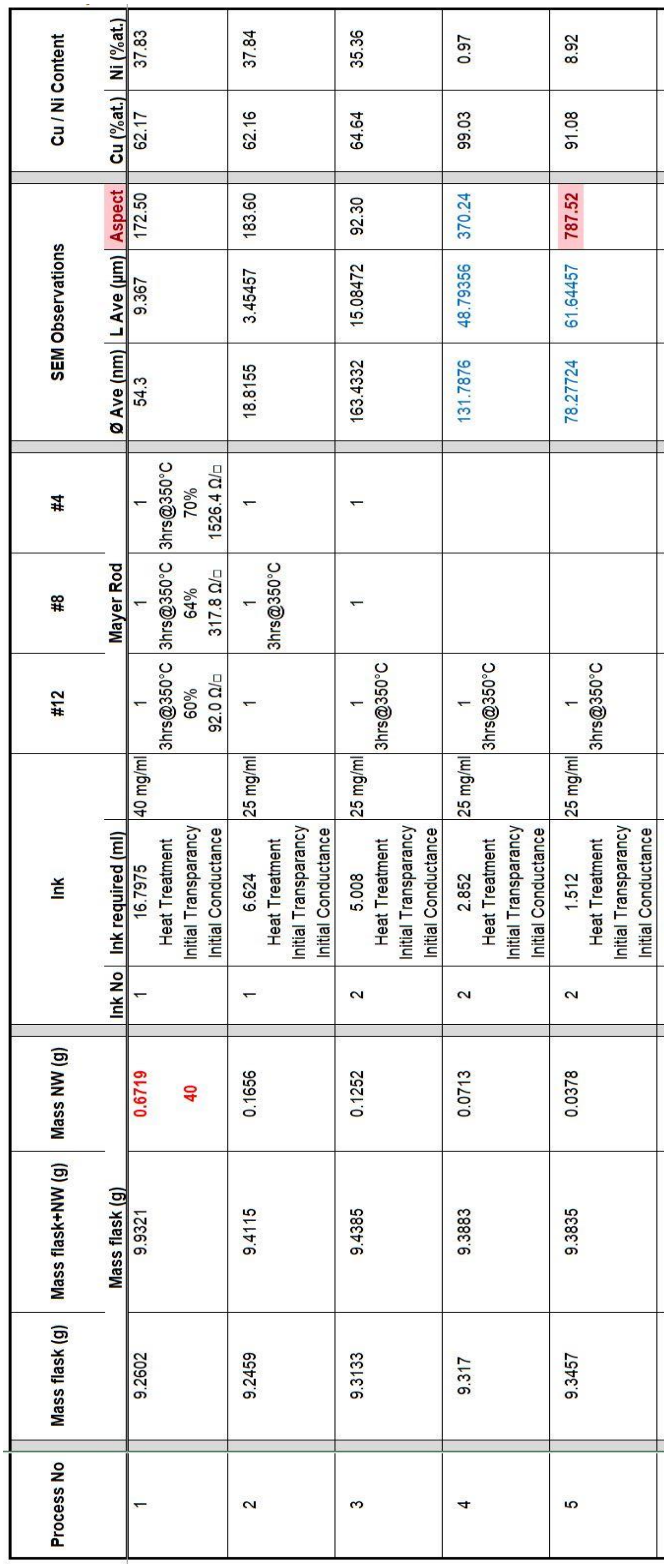
Process No	Date	Chemical	Volume (ml)	Molar Mass M (g.mol^{-1})	Mass (g)		Mass (g)	Number of Moles n (mol) n = m/M n = C.V	Concentration (mol.L^{-1}) C = n/V
			Theory		Glucose	Volume (ml)			
1	26/03/2018	D-(+)-Glucose $C_6H_{12}O_6$		180.16	0.5		0.5001	0.002775926	0.111037027
		Copper (II) chloride dihydrate $CuCl_2.2H_2O$		170.48	0.4092		0.4091	0.002399659	0.095986358
		Nickel(II) acetate tetrahydrate $Ni(C_2H_3O_2)_2.4H_2O$		248.84	0.2986		0.2985	0.001199553	0.047982115
		Oleylamine $C_{18}H_{37}N$ (solvent)	25	267.49	20.325	25	20.325	0.07598307	3.039322781
2	03/04/2018	D-(+)-Glucose $C_6H_{12}O_6$		180.16	0.25		0.2501	0.00138824	0.055529615
		Copper (II) chloride dihydrate $CuCl_2.2H_2O$		170.48	0.4092		0.4091	0.002399659	0.095986358
		Nickel(II) acetate tetrahydrate $Ni(C_2H_3O_2)_2.4H_2O$		248.84	0.2986		0.2986	0.001199955	0.047998189
		Oleylamine $C_{18}H_{37}N$ (solvent)	25	267.49		25	20.325	0.07598307	3.039322781
3	10/04/2018	D-(+)-Glucose $C_6H_{12}O_6$		180.16	1		1.0003	0.005552406	0.222096257
		Copper (II) chloride dihydrate $CuCl_2.2H_2O$		170.48	0.4092		0.4092	0.002400246	0.096009821
		Nickel(II) acetate tetrahydrate $Ni(C_2H_3O_2)_2.4H_2O$		248.84	0.2986		0.2988	0.001200758	0.048030338
		Oleylamine $C_{18}H_{37}N$ (solvent)	25	267.49		25	20.325	0.07598307	3.039322781
4	11/04/2018	D-(+)-Glucose $C_6H_{12}O_6$		180.16	0.125		0.1257	0.000697728	0.027909127
		Copper (II) chloride dihydrate $CuCl_2.2H_2O$		170.48	0.4092		0.4091	0.002399659	0.095986358
		Nickel(II) acetate tetrahydrate $Ni(C_2H_3O_2)_2.4H_2O$		248.84	0.2986		0.2987	0.001200357	0.048014264
		Oleylamine $C_{18}H_{37}N$ (solvent)	25	267.49		25	20.325	0.07598307	3.039322781
5	12/04/2018	D-(+)-Glucose $C_6H_{12}O_6$		180.16	0.2		0.1998	0.001109038	0.044361524
		Copper (II) chloride dihydrate $CuCl_2.2H_2O$		170.48	0.4092		0.4095	0.002402005	0.096080209
		Nickel(II) acetate tetrahydrate $Ni(C_2H_3O_2)_2.4H_2O$		248.84	0.2986		0.2986	0.001199955	0.047998189
		Oleylamine $C_{18}H_{37}N$ (solvent)	25	267.49		25	20.325	0.07598307	3.039322781

Table 28 Spreadsheet of Data Part 1 (Repeat of Table 4)



Process No	Molar ratio n(Cu)/n(Ni)	Density ρ (g/cm^3)	Amb Temp (°C)	Humid. (%)	Pre-Heat (°C / min)	By	Hex	IPA	AA	By		Temp (°C)	Event	Time (hrs)
					Heating		Cleaning							
1	2.0005	1.2 3.6 1.54 0.813	?	?	95 / 30	QL	3	2+3	1	QL		195	QL	16
2	1.9998	1.2 3.6 1.54 0.813	?	?	95 / 30	PK	3	2+3	1	PK		195		16
3	1.9989	1.2 3.6 1.54 0.813	20	?	95 / 30	PK	3	2+2+4	1+1	PK		195		16
4	1.9991	1.2 3.6 1.54 0.813	19.7	38	95 / 30	PK	3	1+3+3	2	PK		195 °C		16
5	2.0017	1.2 3.6 1.54 0.813	19.4	40	95 / 30	AJ	3	2+3	1	AJ		190	AJ	20

Table 29 Spreadsheet of Data Part 2



Process No	Mass flask (g)	Mass flask+NW (g)	Mass NW (g)	Ink			#12	#8	#4	SEM Observations			Cu / Ni Content	
		Mass flask (g)		Ink No	Ink required (ml)			Mayer Rod		Ø Ave (nm)	L Ave (µm)	Aspect	Cu (%at.)	Ni (%at.)
1	9.2602	9.9321	0.6719 40	1	16.7975 Heat Treatment Initial Transparancy Initial Conductance	40 mg/ml	1 3hrs@350°C 60% 92.0 Ω/□	1 3hrs@350°C 64% 317.8 Ω/□	1 3hrs@350°C 70% 1526.4 Ω/□	54.3	9.367	172.50	62.17	37.83
2	9.2459	9.4115	0.1656	1	6.624 Heat Treatment Initial Transparancy Initial Conductance	25 mg/ml	1	1 3hrs@350°C	1	18.8155	3.45457	183.60	62.16	37.84
3	9.3133	9.4385	0.1252	2	5.008 Heat Treatment Initial Transparancy Initial Conductance	25 mg/ml	1 3hrs@350°C	1	1	163.4332	15.08472	92.30	64.64	35.36
4	9.317	9.3883	0.0713	2	2.852 Heat Treatment Initial Transparancy Initial Conductance	25 mg/ml	1 3hrs@350°C			131.7876	48.79356	370.24	99.03	0.97
5	9.3457	9.3835	0.0378	2	1.512 Heat Treatment Initial Transparancy Initial Conductance	25 mg/ml	1 3hrs@350°C			78.27724	61.64457	787.52	91.08	8.92

Table 30 Spreadsheet of Data Part 3