

A Study on the Fabrication of Seamless Semiconducting and Metallic Nanowire Networks and their Applications for Transparent Electronics



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for the degree of
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by

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Declaration

I, the undersigned, declare that this work has not previously been submitted as an exercise for a degree at this, or any other University, and that unless otherwise stated is my own work. Elements of this work that have been carried out jointly with others or by collaborators have been duly acknowledged in the text. I agree to deposit this thesis in the University's open access institutional repository or allow the library to do so on my behalf, subject to Irish Copyright Legislation and Trinity College Library conditions of use and acknowledgement.

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S u m m a r y

Devices based on one dimensional materials have demonstrated remarkably high performance across a wide range of applications, however the commercialisation of these technologies is limited by the difficulties associated with the precision placement and electrical contacting of individual nanostructures. Networks of nanowires have been studied in the hopes of manifesting the desirable characteristics of one dimensional materials on a more easily processed scale. The form factor of nanowire networks also affords the device properties of flexibility and optical transmission which enables their utilisation in next generation transparent and flexible electronics. However, the performance of network based devices has not matched that reported for individual nanowires. This is due to the significant contact resistances present at junctions between nanowires which dominate the electrical behaviour of the device. This thesis focusses on addressing this issue through the development of new fabrication techniques for interconnected nanowire networks with seamless junctions and also examines their performance as components for transparent electronics.

Chapter 3 details the fabrication of silicon nanowire networks with continuous junctions from a silicon-on-insulator wafer and investigates their application as transparent photodetectors. Patterning of the SOI precursor was accomplished using a crack lithography process which exploited the fracturing behaviour of drying colloidal films to form a percolative void network. An interconnected metal etch mask was patterned over the surface of the substrate through physical vapour deposition using the cracked film as a deposition template. Removal of the crack template was performed in organic solvent and a plasma etch process was used to map the metal network pattern onto the underlying silicon device layer. The removal of the metal mask was accomplished using a series of selective chemical etches and SEM analysis of the silicon network allowed the number of disconnected nanowire sections to be quantified. A float transfer process utilising a photoresist mesh support was developed to mount the silicon network on a transparent and flexible PET substrate. A metal assisted chemical etch process was performed to introduce a

random pattern of localised porous silicon regions within the single crystal network. Optical and electrical characterisation was carried out and the device demonstrated high performance as a photodetector alongside optical transparency across the visible spectrum. Comparison against an unporosified crystalline silicon network showed enhanced UV absorption which was attributed to quantum confinement effects within the nanocrystalline silicon present around the pore sites. Low temperature studies showed evidence for a variable range hopping mechanism and the observed photoconduction behaviour was attributed to charge carrier hopping between localised trap states. Stable device performance was demonstrated over 1000 flexing cycles up to a bending radius of 5 mm. In comparison with literature publications, these porous silicon networks ranked among the highest performing transparent photodetector devices reported to date.

Chapter 4 describes the development of a patterning strategy for the formation of a deposition template mapped from the structure of electrospun nanofibres. The performance of templated aluminium nanowire networks as transparent conductors is also investigated. An electrospinning process was optimised for the production of uniform PMMA nanofibres from a CTAB-DMF solvent system. PMMA nanofibres were deposited on PS coated substrates and ebeam deposition was performed to map a negative pattern of the network onto the underlying film. An acetic acid development selectively removed the PMMA nanofibres and left the patterned structure unaffected. The final template structure was formed using an oxygen plasma to etch the unmasked PS areas and expose the underlying substrate. Comparison of the dimensions of templated metal structures against the original PMMA nanofibres using SEM analysis demonstrated the high fidelity of this pattern transfer process. Templated aluminium networks were fabricated and displayed comparable performance to the best reported transparent conductor materials from literature. Notably, these networks are the first aluminium based materials to outperform thin films of indium tin oxide, the current industry standard transparent conductor. In addition to their high transmission/conductivity figure of merit, these aluminium networks also offer a lower raw material cost and demonstrate high stability against corrosion.

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List of Abbreviations

AFM	Atomic Force Microscope
BOX	Buried Oxide
BSE	Back Scattered Electrons
CCD	Charge Coupled Device
CMOS	Complementary Metal Oxide Semiconductor
CNT	Carbon Nanotube
cSi	Crystalline Silicon
CTAB	Cetyltrimethylammonium bromide
CVD	Chemical Vapour Deposition
DI H ₂ O	Deionised Water
DUT	Device Under Test
EBL	Electron Beam Lithography
EDX	Electron Dispersive X-ray Spectroscopy
EQE	External Quantum Efficiency
ICP	Inductively Coupled Plasma
Inlens	Inlens Detector
IR	Infrared
ITO	Indium Tin Oxide
IV	Current-Voltage
LED	Light Emitting Diode
MACE	Metal Assisted Chemical Etch
NFN	Nanofibre Network
NWN	Nanowire Network
OCS	Carbonyl Sulfide
PET	Polyethylene Terephthalate
pSi	Porous Silicon
PVC	Passive Voltage Contrast

PVP	Polyvinyl Pyrrolidone
RF	Radio Frequency
RIE	Reactive Ion Etch
SAED	Selective Area Electron Diffraction
SE	Secondary Electron
SE2	Secondary Electron Detector
SEM	Scanning Electron Microscope
SOI	Silicon on Insulator
STM	Scanning Tunnelling microscope
TC	Transparent Conductor
TEM	Transmission Electron Microscope
UV	Ultraviolet
VLS	Vapour Liquid Solid
VRH	Variable Range Hopping

Publications and Presentations

Publications

M. Hossain, G.S. Kumar, S.N. Barimar Prabhava, **E.D. Sheerin**, D. McCloskey, S. Acharya, K.D.M. Rao, and J.J. Boland, '*Transparent, Flexible Silicon Nanostructured Wire Networks with Seamless Junctions for High-Performance Photodetector Applications*,' ACS nano, 12(5), pp.4727-4735 (2018).

Poster Presentations

'Single Crystal Silicon Nanowire Networks with Seamless Junctions'

MRS Fall Meeting

(Boston, United States of America, November 2017).

Oral Presentations

'Monocrystalline interconnected silicon networks and their photovoltaic behaviour'

Trinity College/University College Dublin DubChem 3rd year Postgraduate Talk,

(Dublin, May 2017)

'Seamless Aluminium Nanowire Networks as High Performing Transparent Conductors'

Finalist in the Trinity College Dorgan competition,

(Dublin, Ireland, September 2018)

'It's of no use whatsoever...'

-Heinrich Hertz, on his discovery of radio waves.

1

Introduction

“I would like to describe a field, in which little has been done, but in which an enormous amount can be done in principle...a point that is most important is that it would have an enormous number of technical applications. What I want to talk about is the problem of manipulating and controlling things on a small scale.” - Richard P. Feynman, 1959.

At the annual meeting of American Physical Society at the California Institute of Technology in December 1959, the great physicist Richard Feynman addressed the scientific community and gave his now famous lecture entitled ‘There’s plenty of room at the bottom’.¹⁻² He discussed how it could be possible to ‘write’ all 24 volumes of the *Encyclopaedia Britannica* on the head of a pin by manipulating individual atoms; illustrating the immense technological potential that could be harnessed if only we had the ability to control matter on the atomic scale. Feynman’s vision far surpassed the capabilities of his day as atomic resolution imaging did not become feasible until tools such as the scanning tunnelling microscope (STM) and atomic force microscope (AFM) were developed in the 1980s.³⁻⁴ The introduction of these and other advanced characterisation techniques⁵⁻⁶ has allowed the optical diffraction resolution limit to be bypassed and has made possible the direct visualisation and study of nanoscale materials.

While the phrase ‘nano’ does not explicitly feature in Feynman’s lecture, it is fair to say that the current field of nanoscience takes inspiration from his vision and collectively works toward its realisation. Nanoscience is a broad interdisciplinary field which generally refers to the study of materials with any dimension smaller than

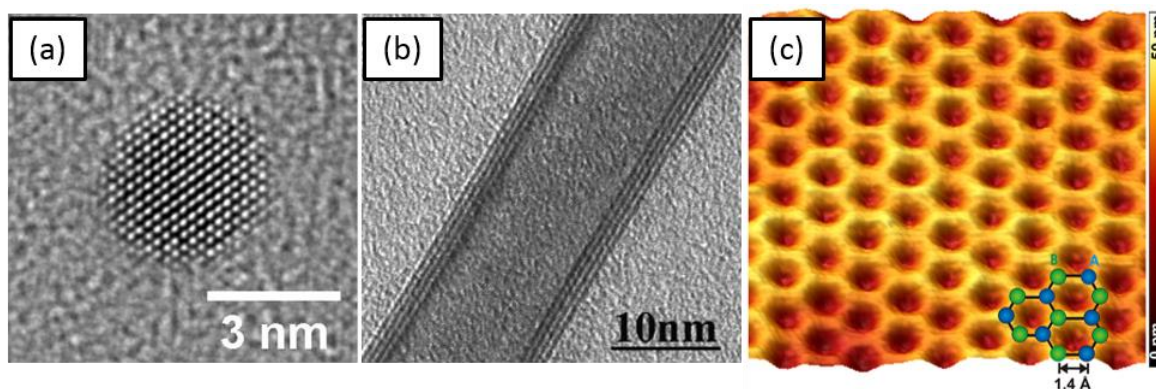


Figure 1.1. Transmission electron microscope image of (a) platinum nanoparticle,⁷ (b) multiwalled carbon nanotube⁸ and (c) Scanning tunnelling microscope topography image of a graphene monolayer.⁷

100 nanometres (1 nm = 1 billionth of a metre). Substantial deviations from bulk material properties observed at this length scale have generated considerable interest in exploiting nanostructures for device applications.⁹⁻¹¹ These size dependant effects are due in part to the increasing ratio of surface to bulk atoms as a structures size is reduced to nanoscale dimensions. Interfacial atoms can contain dangling bonds or display disordered structures in contrast to atoms within the bulk which universally exist within a homogenous close packed environment.¹² In the case of a large particle, surface atoms represent a small minority of the total number of atoms in the system. However as the diameter of the particle is reduced below 100 nm, the overall percentage of these surface species rapidly increases and begins to appreciably influence the material properties.¹³ For example, a nanoparticle with a diameter of 30 nm has 5% of its atoms present at it's surface; this proportion increases to 20% for a 10 nm particle and 50% for a 3 nm particle.¹⁴ This scaling phenomenon has been exploited for catalytic applications to improve the atom efficiency of large scale industrial processes.¹⁵

The optical and electrical properties of a system can also be strongly influenced by quantum confinement effects when the dimensions of a structure are comparable to it's Bohr radius which is typically on the order of a few nanometres.¹⁶⁻¹⁸ An example of these confinement effects can be seen in CdS quantum dots, whose colour is dependent upon the particle diameter due to the formation of discrete energy levels

within each nanostructure.¹⁹ The demonstration of these novel behaviours has opened up the enticing possibility of using nanoscience to realise a materials by design approach to device fabrication, where the fundamental properties of a material can be controlled and customised to better suit the needs of an application. Nanomaterials can be broadly categorised as either zero dimensional (0D), one-dimensional (1D) or two dimensional (2D) based on their number of macroscopic dimensions. Objects that contain anywhere from tens up to thousands of atoms and are restricted to less 100 nm in all dimensions, such as the nanoparticle shown in figure 1.1 (a) as well as quantum dots, are considered as pseudo 0D. 2D materials display macroscopic length in two dimensions but are limited in the third, these include graphene (figure 1.1 (c)) and analogous inorganic layered materials such as MoS₂ and BN.²⁰⁻²² Structures such as nanowires, nanoribbons and nanotubes are classified as 1D materials; these systems are macroscopic in their length but are limited to the nanoscale in their height and width and it is on these 1D nanomaterials, and specifically on the issue of how best they can be integrated into optoelectronic devices, that this thesis shall focus.

1.1 Nanowires

The discovery of carbon nanotubes (CNTs) reported by Iijima in 1991 sparked the enormous research interest in one dimensional materials which continues to this day.²³ CNTs are hollow tubes of ‘rolled up’ graphene which can exist as either single or multi walled structures as shown in figure 1.1 (b). Their diameters can range from 0.8 nm to upwards of 100 nm depending on the number of walls, and their lengths are typically reported between 10 and a few hundred microns.²⁴ They have high electron mobility²⁵ and can demonstrate either metallic or semiconducting character²⁶ depending on the lattice orientation. An electrostatic discharge shield composed from CNTs was used in NASA’s Juno satellite probe launched in 2011.²⁷ CNTs also possess extremely high tensile strength with values per gram ten to twenty times stronger than that of steel cabling reported for multi walled CNTs,²⁸ and so are widely employed in fibre composite materials for use in boat hulls, wind turbine blades and sports equipment for reinforced strength without adding significant weight.²⁹⁻³⁰ In recent decades, a wide range of synthesis techniques employing both

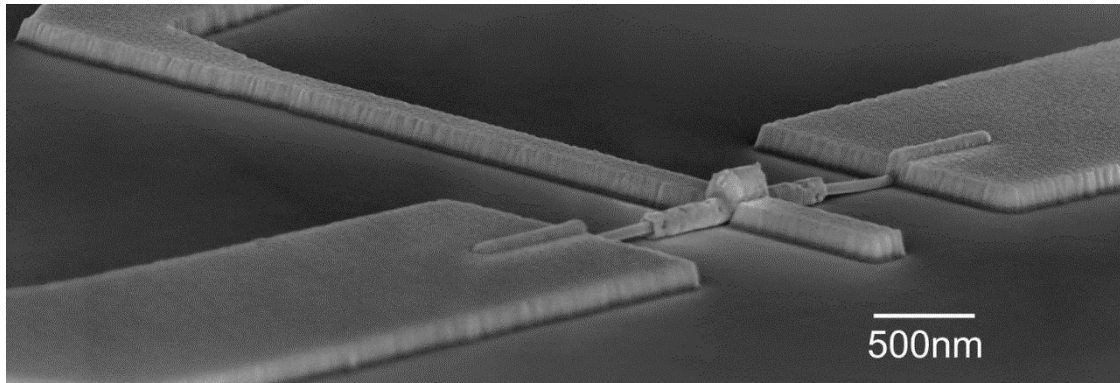


Figure 1.2. EBL contacted individual InAs nanowire with an Al_2O_3 insulated top gate electrode.³¹

solution and vapour processes (polyol-reduction,³² vapour-liquid-solid (VLS) growth,³³ template deposition³⁴) have been developed and optimised to facilitate the fabrication and study of other one dimensional structures with controlled morphologies³⁵⁻³⁷ and material compositions.³⁸⁻⁴⁰

The channel-like character of nanowires makes these structures well suited for conductivity modulation and their small size allows for extremely high density device arrays. Figure 1.2 is an SEM image of a top gated transistor based on a single InAs nanowire and analogous individual nanowire devices with electron beam lithography (EBL) defined contacts have been investigated for a diverse range of applications. Memory storage systems,⁴¹ optical and chemical sensors⁴²⁻⁴³ as well as electromechanical switches⁴⁴ have been demonstrated with high sensitivities, fast response times and small device footprints.^{43, 45-51} Despite these promising results, the commercialisation of single nanowire technologies has yet to be realised which can be attributed to the extreme difficulties associated with reproducibly making electrical contact to isolated 1D nanostructures. The tedious alignment and slow direct write patterning steps required for their fabrication prevents the widespread integration of these technologies.⁵²⁻⁵⁴

1.1.1 Nanowire Networks

Networks of randomly deposited nanowires have been studied in the hopes of accessing the desirable optical and electronic characteristics demonstrated by single

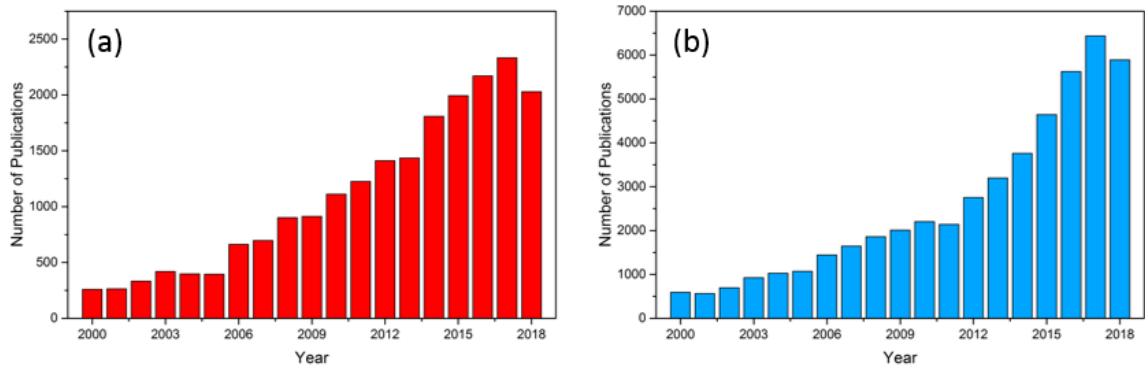


Figure 1.3. Number of publications per year containing the terms (a) “Transparent electronics” (b) “Flexible electronics” collated from Web of Science.⁵⁵

nanowire based devices in a larger scale system.⁵⁶⁻⁵⁷ The increased area of the network removes the reliance upon slow and costly EBL based fabrication methods as contacting can be performed using lower resolution but significantly higher throughput techniques such as UV lithography which is capable of wafer scale patterning on timescales of minutes rather than tens of hours.⁵⁸ Structural variations between individual nanowires are also averaged out when processed into a network resulting in more reliable and predictable device behaviour based on nanowires mean properties. Additionally, the structural form of nanowire networks (NWN) is naturally well suited for device applications requiring transparency and flexibility. The optical transmission of the network is determined by the nanowire area density and is relatively independent of their material composition which allows for access to a wide range of device functionalities alongside optical transparency.⁵⁹⁻⁶³ NWNs are not subject to the same mechanical degradation modes as films and networks of nanowires composed of normally brittle materials have demonstrated highly stable performance over many thousands of bending cycles.⁶⁴⁻⁶⁷ The motivation for faster, smaller and more powerful electronics has been the driving force behind the progress of the microelectronics industry over the last century and this same motivation continues to this day. A serious demand for additional device functionalities has now also developed as evidenced by the rapid growth in research publications concerning these properties illustrated in figure 1.3 and NWNs could offer a versatile design strategy for the fabrication of high performing next generation devices.

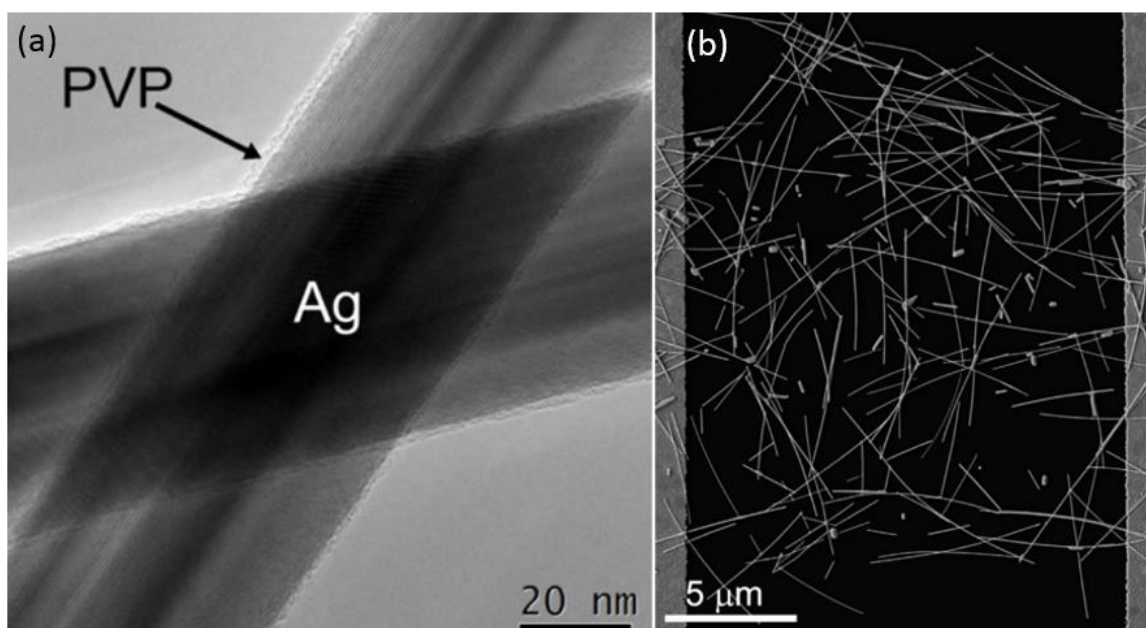


Figure 1.4. (a) TEM image of a junction between two PVP coated silver nanowires (b) SEM image of a silver nanowire network.⁶⁸

NWNs can be easily fabricated over large areas using solution based deposition techniques such as Meyer rod, dip or spray coating.⁶⁹⁻⁷¹ However in order to form a stable suspension for processing, the nanowires must be coated with a passivation layer to prevent cold welding and flocculation out of solution.⁷²⁻⁷³ These surface coatings typically consist of either poorly conducting oxides or polymers and result in large contact resistances between intersecting nanowires within the network.⁷⁴ Figure 1.4 (a) is a TEM micrograph of two overlapping polyvinylpyrrolidone (PVP) coated silver nanowires and this image illustrates the minimal contact area which also contributes toward the contact resistance. Direct measurements of junction resistances have been performed for a number of nanowire systems and their impact on the overall device behaviour has been well studied.^{68, 75} Post treatment steps such as annealing, electroforming or plasmonic welding are often used to improve connectivity within NWNs but junction resistances are not fully eliminated even after these aggressive processes.^{59, 76-77} The existence of highly resistive junctions have prevented NWNs from exploiting the full potential of one dimensional nanostructures demonstrated in individual nanowire devices.^{42, 78} In order to maximise the performance of NWNs it is therefore necessary to reduce the impact of junctions on the electrical behaviour of the device. This work aims to

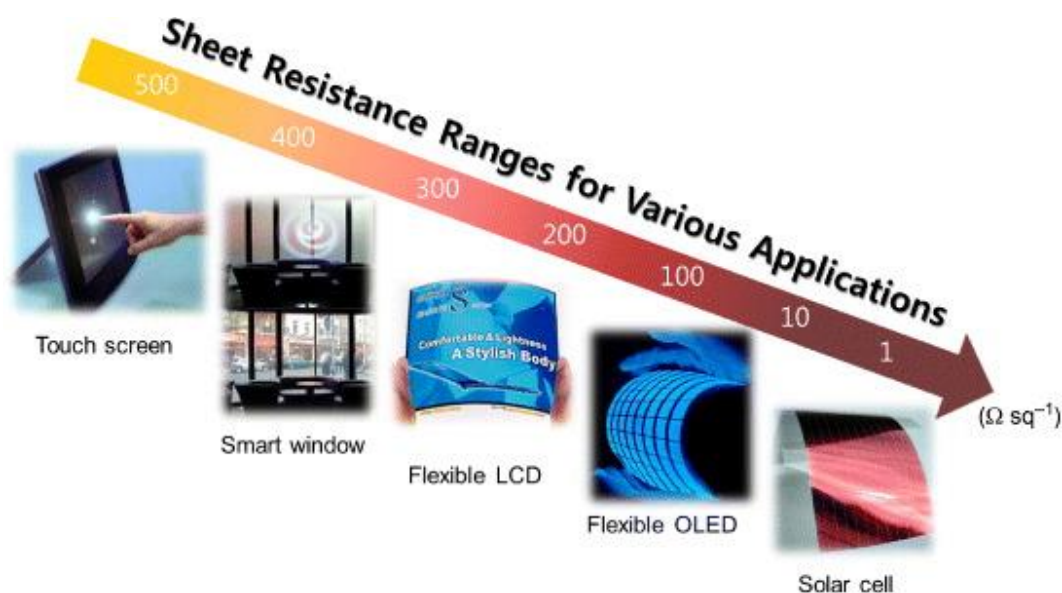


Figure 1.5. General sheet resistance requirements for a selection of industrially important transparent conductor applications.⁷⁹

develop fabrication strategies for NWNs with seamless junction geometries and investigate their performance as optimised optoelectronic devices.

1.2 Transparent Conductors

Materials which demonstrate the unique combination of optical transparency and electrical conductivity are known as transparent conductors (TCs) and are essential components in a wide range of everyday technologies. The functionality of solar cells, light emitting diodes (LEDs), transparent heaters, capacitive and resistive touchscreens as well as many other device types depend upon high performing TC coatings.⁸⁰⁻⁸³ Figure 1.5 illustrates the general range of sheet resistances required for a selection of major applications. Certain devices such as solar cells and LEDs simply require as low a sheet resistance as possible to maximise their overall efficiency.⁸⁴ While other applications have a defined range in which they can operate, capacitive touchscreens for instance require sheet resistances between 100-500 ohm/sq.⁸³ Virtually all applications demand the maximum possible transparency and there are many other material property requirements (work function,⁸⁵ haze,⁸⁶ thermal stability,⁸⁷ flexibility,⁸⁸ etc...) in addition to sheet resistance which are specific to each application and ultimately dictate the choice of TC material.

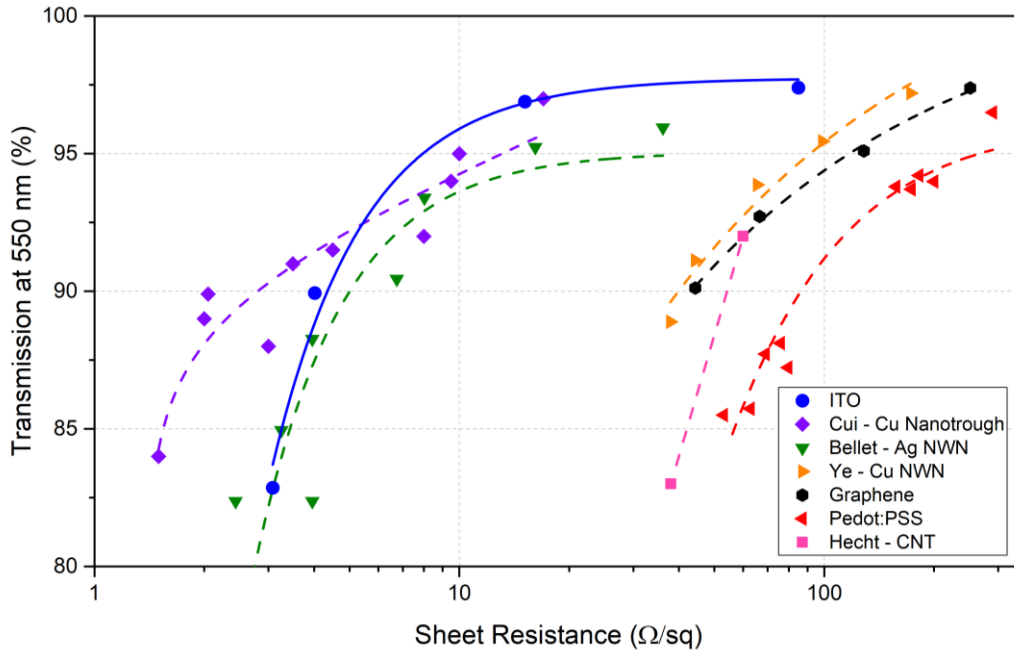


Figure 1.6. Performance of ITO thin films and a selection of top reported transparent conducting materials from literature.^{66, 81, 89-92}

Light transmission at visible wavelengths indicates the presence of a large energy gap separating a materials valence and conduction bands. This relationship is shown in equation (1) where λ is wavelength (nm), h is planks constant (eV.s), c is the speed of light in vacuum (nm/s) and E_g is the band gap (eV) of the material.

$$\lambda = \frac{hc}{E_g} \quad (1)$$

For instance, quartz has a band gap of 6.3 eV and demonstrates high transparency to wavelengths down to 200 nm.⁹³ This large energy gap is also responsible for the extremely low electrical conductivity of quartz as appreciable numbers of valence electrons cannot transition into the empty conduction band under standard conditions.⁹⁴ Semiconductors with sufficiently large band gaps can also display transparency to visible light and certain metal oxides such as ZnO, SnO₂ and In₂O₃ fall under this category with bandgaps ranging from 3.7 eV to 4.1 eV.⁹⁵⁻⁹⁹ Relatively high values of conductivity can be obtained through doping these materials to shift the fermi level upwards into the conduction band.¹⁰⁰ By far the most commonly

employed metal oxide in the TC industry is indium tin oxide (ITO) as thick, high quality films of indium oxide degenerately doped with tin can display resistivities of only a few ohm/sq and transmittance values above 90% at 550 nm.¹⁰¹ As shown in figure 1.6, the sheet resistance of ITO films can be tuned across a wide range by controlling the film thickness which has resulted in the widespread integration of ITO across a diverse range of TC applications.

ITO films suffer from a number of notable disadvantages however; firstly, the global scarcity of indium reserves has resulted in high and unstable raw material costs¹⁰² and the final device price is further increased by the slow, high temperature sputtering process required for the fabrication of high quality films. ITO displays poor UV transparency as a result of its ~ 4 eV band gap and also has limited transmission over IR wavelengths, properties which have a detrimental effect on the overall efficiency of devices such as solar cells.¹⁰³ Additionally, ITO films are extremely brittle, demonstrating mechanical fracturing and large increases in sheet resistance under even mild strain which prevents their use in flexible electronics.¹⁰⁴ These and other disadvantages have motivated extensive research into alternative TC materials with better sustainability, lower cost and additional functionalities.

1.2.1 Polymers

Certain organic polymers such as polyindole,¹⁰⁵ PEDOT:PSS¹⁰⁶⁻¹⁰⁷ and polypyrrole¹⁰⁸⁻¹⁰⁹ demonstrate semiconducting properties as a result of delocalised π -electrons along their conjugated backbones and have been studied as active electrode materials for plastic electronics. Their optical and electrical properties can be controlled through structural modifications of the polymer chains and this behavioural range had allowed the fabrication of complex devices such as transistors,¹¹⁰⁻¹¹¹ LEDs¹¹²⁻¹¹³ and solar cells¹¹⁴⁻¹¹⁵ from all-organic and transparent components. This diversity of optoelectronic properties gives polymers a unique advantage in terms of device functionality over TC metal oxides which are mostly limited to n-type semiconducting behaviour.^{96, 116} However, conductive polymers typically demonstrate poor thermal stability at temperatures above 120°C and, in terms of

absolute TC performance, they remain firmly behind most other materials for low sheet resistance applications.¹¹⁷⁻¹¹⁸

1.2.2 Graphene and CNTs

Graphene has attracted interest as a potential TC material owing to its high optical transmittance and mobility in its monolayer form.¹¹⁹⁻¹²¹ The best reported doped films grown by chemical vapour deposition (CVD) have demonstrated sheet resistances of $\sim 125/n \text{ } \Omega/\text{sq}$ and transmittances of $100-(2.3n)\%$ where n is the number of graphene layers.¹²² As shown in figure 1.6, monolayer and few layer graphene devices fall short in comparison to the performance of ITO but would still be suitable for certain applications. However, difficulties associated with the large scale production of graphene currently limit its utility as a TC material. Mechanical exfoliation from bulk graphite can produce high quality flakes but this methodology does not scale up to the areas necessary for most applications.¹²³ CVD on copper surfaces can produce relatively large graphene films which can then be stamp transferred onto alternative substrates, although poor substrate adhesion and the risk of damage during transfer remain significant issues.¹²⁴

CNTs have also been proposed as potential TC materials due to the high mobilities and conductivities reported for individual CNT devices.¹²⁵ However, the large junction resistances present between nanotubes in percolative networks of CNTs have greatly limited the performance of these materials as TCs.¹²⁶ The best reported data from Hecht *et al.* relied upon harsh processing conditions employing a super acid as a solvent for solution deposition onto a polymer substrate and the overall device performance still lagged behind that of graphene based devices.⁹²

1.2.3 Nanowire Networks

The TC materials discussed thus far; ITO, graphene and conducting polymer films all represent an approach to TC design that requires achieving a compromise between the diametrically opposed material properties of optical transparency and electrical conductivity. An alternative approach is to pattern a substrate with an opaque but

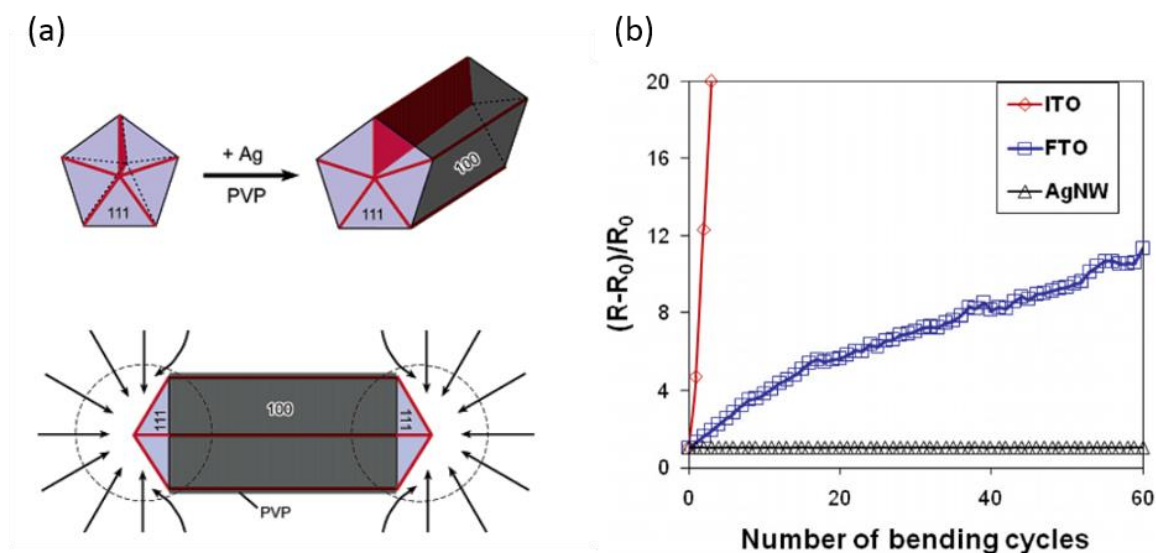


Figure 1.7. (a) Schematic of pentagonally twinned silver nanowire polyol growth process.³² (b) Sheet resistance of ITO, FTO and silver nanowire networks over 60 bending cycles to a radius of 5 mm.⁶⁶

highly conductive material arranged in a grid structure with regularly spaced openings to allow for optical transmission. This device form factor can be realised through percolative networks of metallic nanowires as shown in figure 1.4 (b). Solution based synthesis techniques have been developed and optimised such that high quality crystalline nanowires made from conductive metals such as silver and copper can be produced on a large scale.^{32, 127} Simple deposition techniques such as dip, rod and spray coating allow networks to be produced over large areas, and furthermore the sheet resistance of the network can be easily tuned to the desired range through variation of the nanowire area density. Silver NWNs have also demonstrated greatly improved stability under flexing tests over oxide based TCs as shown in figure 1.7 (b).

Figure 1.6 illustrates the performance of silver and copper nanowire networks (NWNs) alongside that of ITO and a selection of other TC materials. It can be seen that silver NWNs closely approach the performance of ITO while copper based networks rank slightly further behind. While the bulk resistivity of copper is only 6% higher than silver, its greater tendency towards ambient oxidation results in large junction resistances which are responsible for the decreased performance of Cu NWNs.¹²⁸⁻¹³² For the purposes of this introduction, this discussion shall focus

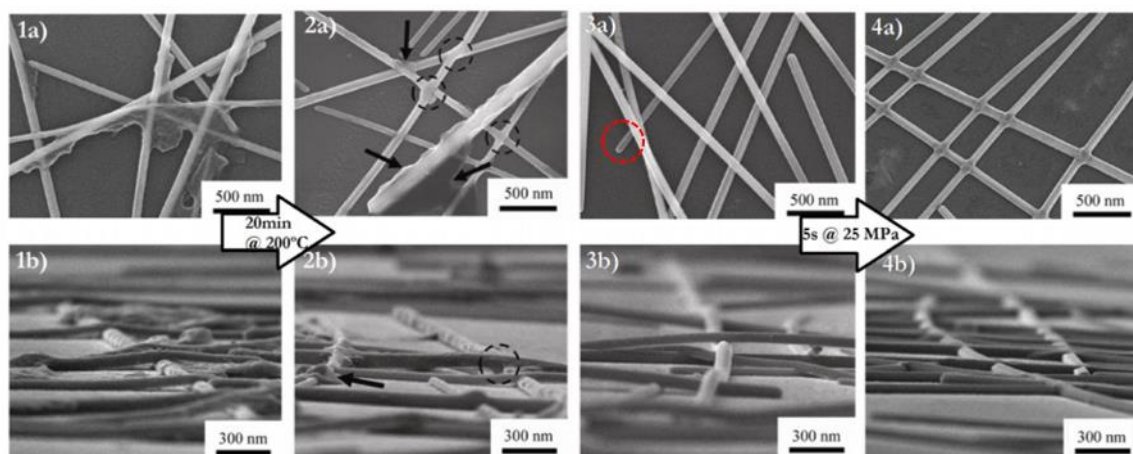


Figure 1.8. SEM images of silver NWNs: 1 (ab) spray deposited network, 2 (ab) thermally annealed network at 200°C for 20 min, 3 (ab) spray deposited network rinsed in water and ethanol with dangling nanowire section highlighted and 4 (ab) mechanically pressed network at 25 MPa for 5s.⁶⁶

primarily on high performing networks of pentagonally twinned silver nanowires fabricated using the polyol synthesis technique. A schematic of the polyol growth process is shown in figure 1.7 (a), silver nitrate is reduced by ethylene glycol in the presence of PVP which selectively interacts with the $\langle 100 \rangle$ crystal facets and promotes anisotropic growth along the $\langle 111 \rangle$ direction.^{32, 133} Polyol synthesised nanowires exhibit a thin uniform PVP shell which can be seen in the TEM micrograph in figure 1.4 (a), and when processed into a network this polymer coating acts an insulating barrier between nanowires. Consequently, as deposited NWNs display high sheet resistances and post processing steps such as thermal annealing¹³⁴ or mechanical pressing⁷⁴ are commonly used; examples of NWNs before and after these treatments are shown in figure 1.8. These aggressive processes restrict the available choice of substrate and studies on individual junctions have shown that they do not fully eliminate contact resistances between nanowires.⁶⁸ Alternative methods such as plasmonic welding of junctions using high energy broadband light sources have only resulted in modest improvements in conductivity.⁷⁶

In addition to junction resistance limited network connectivity, dangling wire segments as highlighted in figure 1.8 (3a) do not contribute to electrical conduction but reduce the total optical transmission of the network. Image analysis on silver NWNs performed by Kulkarni *et al.* estimated the percentage of network area

coverage comprised of dangling sections and isolated nanowires at 32%.¹³⁵ It has also been shown that increasing the nanowire aspect ratio can improve device performance through minimising the number of junctions necessary to form a percolative pathway and increasing the number of contact points between wires.¹³⁶

Another significant issue concerning Ag NWNs is the susceptibility of silver to corrosion from atmospheric sulfur compounds.¹³⁷⁻¹⁴⁰ Sulfur containing species can originate from either natural sources or from the combustion of fossil fuels and have been detected at high levels globally.¹⁴¹⁻¹⁴² Studies on the sulfidation of PVP coated silver nanowires under ambient conditions of temperature and humidity have shown that significant corrosion can occur over a timescale of weeks.¹⁴³ The reactivity of nanostructured silver raises doubts about the long term reliability of devices based on these materials and highlights the need for additional protective measures.¹⁴⁴ Ag NWNs represent a high performing but as yet unoptimised TC device type; post processing treatments and optimisation of the nanowire dimensions can only minimise, but not completely eliminate, the detrimental effects of junction resistances and inactive wire segments on device performance.

1.2.3.1 Seamless Networks

The highest performing TC materials reported thus far have been NWNs fabricated with seamless junctions such as electrospun fibre templated nanotroughs⁹⁰ and larger scale metal grids defined using techniques such as crack lithography.¹⁴⁵ The latter technique exploits the cracking tendency of drying colloidal films to form an interconnected template for metal deposition and is discussed in detail in chapters 2 and 3. Seamless networks of wires with widths ranging from 6 μm down to under 1 μm can be fabricated using crack lithography, and silver crack networks have demonstrated sheet resistances of 0.5 ohm/sq at 83% transmission as well as stable performance under flexing tests.¹⁴⁶ However, an important consideration regarding the use of NWN based TCs is that the measured values of optical transparency and sheet resistances are averages measured over the entire device area and are not uniform at all points across the network. The substrate is completely opaque at the wire locations and resistance is increased within the regions between wires. This is

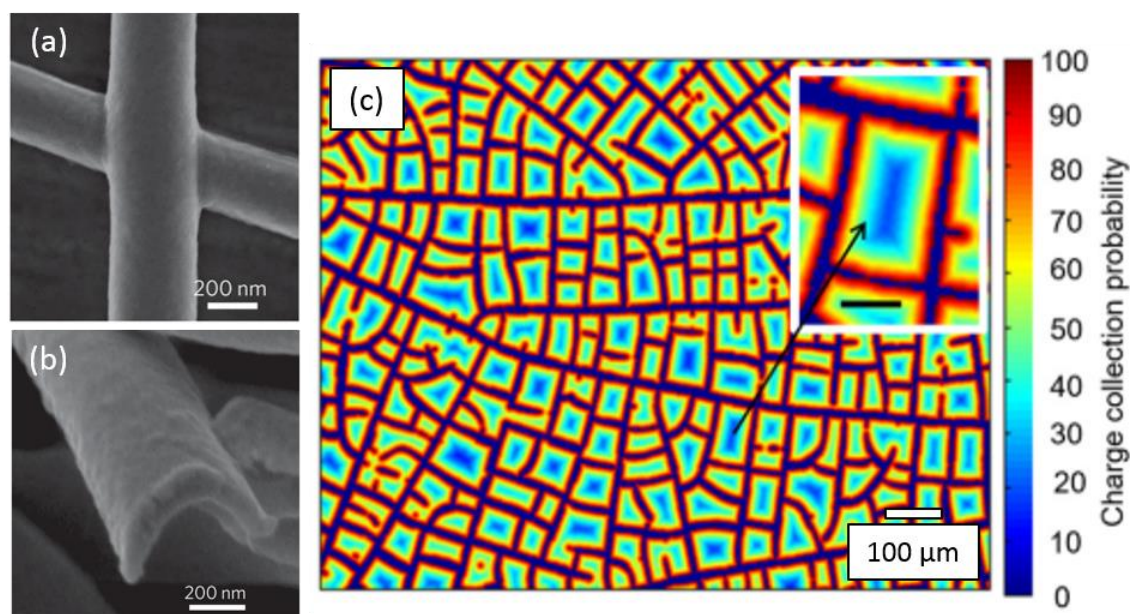


Figure 1.9. SEM images of copper nanotrough networks⁹⁰ (a) top down view of fused junction, (b) edge view of individual nanotrough and (c) simulated charge carrier collection probability map for a crack network calculated for each point based on its distance from the nearest electrode assuming a diffusion length of $20\ \mu\text{m}$.¹⁴⁷

not the case for ITO thin films and has important consequences for the efficiencies of devices such as solar cells and OLEDs which require very low uniform sheet resistances on the scale of the material charge collection length. Figure 1.9 (c) shows a simulated probability map of charge carrier collection for a crack network electrode based on a material with a $20\ \mu\text{m}$ carrier diffusion length.¹⁴⁷ It can clearly be seen that the large openings present in crack templated networks lead to reduced collection probabilities within gaps due to increased carrier recombination. For active materials with high diffusion lengths such as silicon this issue will be less critical, but polymers and perovskites typically have diffusion lengths between $10\ \text{nm}$ and $1\ \mu\text{m}$ which renders crack networks unsuitable for these types of devices.¹⁴⁸⁻¹⁵⁰ Another technique for the fabrication of networks with seamless junctions developed by Cui *et al.* uses electrospun polymer nanofibres as deposition templates to form nanotroughs networks, SEM images of these structures are shown in figure 1.9 (a) and (b). $100\ \text{nm}$ thick copper nanotroughs with an average width of $400\ \text{nm}$ have demonstrated sheet resistances of $2\ \text{ohm/sq}$ at 90% transmittance and excellent stability under strain and flexibility tests.^{90, 151} The narrower diameter of nanotroughs

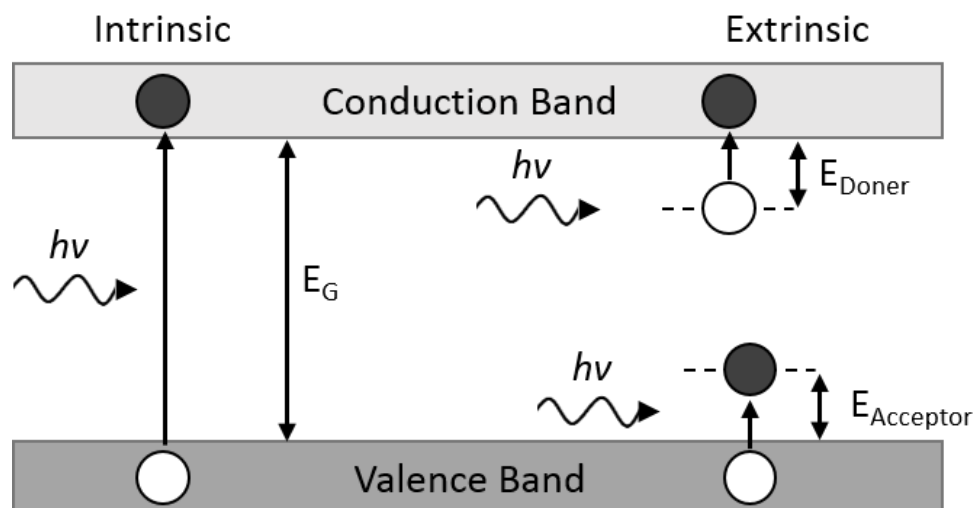


Figure 1.10. Schematic of intrinsic and extrinsic photoexcitation events in a semiconductor.

decreases the average gap area in networks compared to much wider crack templated wires of the same thickness and sheet resistance which reduces carrier recombination losses in solar cells.¹⁵²⁻¹⁵³ However, during electrospinning a ring collector stage is required to form the free standing nanofibre template which limits the maximum device area that can be fabricated.¹⁵⁴ The need for a network transfer step further limits the scalability of this approach. Additionally, the quality of metal deposited through physical vapour techniques strongly depends upon the substrate type and 4 probe measurements on individual nanotroughs showed resistivities significantly above bulk metal values.⁹⁰ While nanotrough networks offer many improvements upon individual NWNs; i.e. continuous junctions, ultra-long wire aspect ratios¹⁵⁵⁻¹⁵⁶ and a wider choice of metals, their relatively large wire widths and poorly scalable fabrication method leave room for further optimisation of seamless NWN systems.

1.3 Photodetectors

A photodetector is a type of optoelectronic sensor which converts an optical signal into an electrical signal through light induced changes in the device conductivity¹⁵⁷. The operation of CCD and CMOS image sensors¹⁵⁸, optical receivers in fibre optic communication systems,¹⁵⁹⁻¹⁶¹ remote control sensors¹⁶² and many other everyday electronic devices all depend on high performing photodetectors. They are typically based on semiconducting materials whose band gap energies correspond to the

Material	Band gap (eV)	Spectral range (nm)
Silicon	1.1	400 -1100
Germanium	0.67	400-1800
InAs	0.36	1000-3800
HgCdTe	~0-1.5	700-25000

Table 1.1. Band gaps and spectral response ranges for a selection of semiconducting materials commonly used in photodetectors.¹⁶³⁻¹⁶⁷

desired wavelength detection range. Many different device constructions are possible but they all operate *via* the photoconductive effect, where electron-hole pairs are generated through the absorption of photons leading to a decrease in the resistance state of the device.¹⁶⁸⁻¹⁷¹ As illustrated in figure 1.10, there are two possible types of absorption events; extrinsic absorption is due to low energy electron transitions between a materials valence or conduction bands and impurity energy levels located within the band gap. Intrinsic absorption refers to the photoexcitation of an electron from the valence band into the conduction band. In direct band gap materials such as InAs, intrinsic absorption requires only a photon with energy equal or greater than the band gap (E_g); whereas for materials with indirect band gaps such as silicon, simultaneous phonon emission or absorption is also necessary for a transition to occur.¹⁷²⁻¹⁷³ The band gaps and wavelength sensitivities of a selection of semiconducting materials commonly used in photodetectors are shown in table 1.1. The incorporation of photodetectors into transparent electronics presents a unique challenge as the device performance inherently requires high optical absorption and therefore necessitates low transmission. Typical bulk semiconductor photodetectors have thick active layers to maximise light absorption and are therefore both brittle and completely opaque.¹⁷⁴⁻¹⁷⁵ Recently, large area transparent and flexible photodetectors have been reported using 2D materials such as graphene, WS_2 and WSe_2 .¹⁷⁶⁻¹⁷⁸ These devices show good transparency and demonstrate large photocurrents but suffer from slow response times on the order of tens of seconds due to short carrier lifetimes.

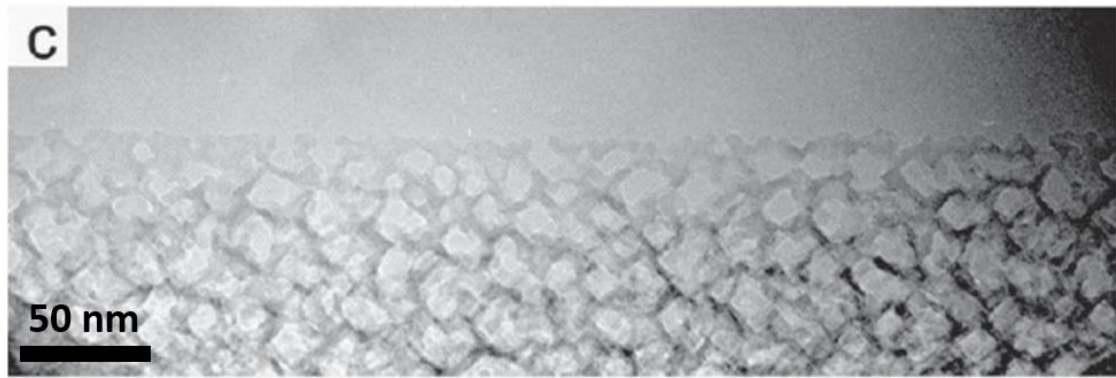


Figure 1.11. TEM micrograph of a pSi shell of a silicon nanowire fabricated through metal assisted chemical etching.¹⁷⁹

Devices based on individual silicon nanowires¹⁸⁰⁻¹⁸² have demonstrated exceptionally high performance as photodetectors, however they are limited to small area applications and the alignment and direct write lithography steps required for their fabrication limit the utility of these technologies. Random percolative networks of semiconducting nanowires¹⁸³⁻¹⁸⁶ have also been reported as transparent and flexible photodetectors but the large contact resistances present at nanowire junctions limit both the photocurrent and response times of these devices. In order to optimise the performance of NWNs for this application, it is therefore essential to use a material that is highly efficient at carrier generation and also to design networks with continuous junction geometries to maximise charge carrier transport.

1.3.1 Porous Silicon

Porous silicon (pSi) was first discovered in 1956 by Uhler and Turner in Bell labs during their investigation of silicon electropolishing.¹⁸⁷ However, widespread interest was only generated in the optoelectronic properties of pSi in 1990 when Canham *et al.* published their report of visible photoluminescence from a pSi structure at much greater efficiencies than possible from bulk silicon.¹⁸⁸ This behaviour was attributed to quantum confinement effects within the porous structure widening the effective band gap of the material. As shown in figure 1.11, the structure of pSi resembles a disordered mesh of silicon nanocrystallites and this material is often referred to as a quantum sponge.¹⁸⁹

The fabrication of pSi structures can be accomplished through either electrochemical anodisation or metal assisted chemical etching (MACE). Anodisation is performed at low current densities in aqueous or ethanol electrolytes at high HF concentrations and generally results in a pSi layer of uniform thickness coating the crystalline silicon surface.¹⁹⁰ In MACE, a silicon substrate is placed in a solution of HF and an oxidative agent which is typically H₂O₂. Porosification occurs at the interface between silicon and a noble metal catalyst such as gold or silver. MACE allows for greater control over the area patterning of pSi formation as silicon which is not coated with noble metals remains relatively unaffected during the etch process. Owing to its high roughness, large surface area and increased energy band gap, pSi demonstrates greatly enhanced optical absorption over bulk silicon especially at high energy UV wavelengths.^{189, 191} The unique optoelectronic properties of pSi have been exploited in applications such as LEDs, photonic logic gates as well as solar cells.^{182, 192-194} In this work, localised pSi sections are selectively introduced into a crystalline silicon NWN using MACE and employed as highly efficient carrier generation sites. The full details of this MACE process and its impact on the performance of the network as a photodetector are discussed in chapter 3.

1.4 Thesis Outline

This chapter has introduced the field of nanoscience and discussed the utility of nanowire networks for next generation optoelectronics as well as challenges in their implementation. The goal of this thesis is to develop new fabrication strategies for interconnected nanowire networks with seamless junctions and to characterise their performance as optimal systems for transparent electronics. Chapter 2 details the working principles behind the many types of equipment and techniques used throughout this work. Chapter 3 describes a methodology for the fabrication of a seamless silicon network through patterning and etching a single crystal silicon on insulator substrate. A transfer process to mount the network on a transparent and flexible polymer substrate is detailed and a metal assisted chemical etch step to introduce discrete zones of porous silicon into the network is discussed. The performance of the porosified network as a transparent and flexible photodetector is investigated and compared against similar devices from literature. Chapter 4

describes the patterning of an interconnected deposition template from a network of electrospun PMMA nanofibres and studies the performance of seamless templated aluminium NWNs as transparent conductors.

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2

Equipment and Methods

The study and manipulation of nanoscale systems is only made possible by the huge advancements in the field of microscopy in recent decades which have allowed us to view and characterise these unprecedentedly small and complex systems. As techniques and equipment become increasingly advanced, it becomes ever more important to have a concise understanding of the theory behind their operation in order to reliably distinguish between what are true signals and the ever present instrumental artefacts. A wide variety of techniques have been employed in this work and the basic operation principles of each are outlined in this section.

2.1 Microscopy

Optical microscopes have long been used in science to study objects too small to be resolved with the naked eye. In 1873, Ernest Abbe discussed the resolving power of light microscopes and predicted a theoretical diffraction limit given by equation (1).

$$d = \frac{\lambda}{2 \sin \theta} \quad (1)$$

Where d is the resolution, λ is the wavelength of light source and θ is the half aperture angle in radians. This was later proven mathematically to be a fundamental limitation of optical microscopy by Helmholtz¹. For visible light the limit of resolving power is predicted to be between 200-350 nm; this theoretical limit also does not take into account the deteriorative effects of noise or aberrations on image quality. Light microscopy therefore does not offer sufficient resolving power for the study of nanoscale systems. In 1924, Louis de Broglie combined Einstein's equation (2) relating matter and energy and Planck's quantum equation (3) relating the frequency

of a wave to its energy. By substituting velocity (v) for the speed of light (c) as shown in equation (4) and substituting velocity/wavelength (v/λ) for frequency (ν) as shown in equation (5) he predicted that any body could be treated as a wave with an associated momentum dependant wavelength given by equation (6).

$$E = mc^2 \quad (2)$$

$$E = h\nu \quad (3)$$

$$mv^2 = h\nu \quad (4)$$

$$mv^2 = \frac{h\nu}{\lambda} \quad (5)$$

$$\lambda = \frac{h}{mv} \quad (6)$$

Where λ is the wavelength, h is Planck's constant and m and v are the mass and velocity of the particle respectively. Electrons with sufficiently high velocities can have associated wavelengths far lower than those of visible light. A typical scanning electron microscope (SEM) accelerating voltage of 10 kV corresponds to a wavelength of 12.2 pm and a theoretical resolution of 6.1 pm. This limit places the resolving power of a SEM well below the atomic scale, however aberrations in the electromagnetic lenses coupled with beam damage and other sample interactions prevent the achievement of such high resolution². Even when taking these additional limitations into account, the maximum resolving power of optical microscopy can be routinely surpassed with even the most basic of electron microscope setups³. Despite their limitations, optical microscopes are still of crucial importance in the modern field of nanoscience, offering a simple and non-destructive route to basic sample analysis unmatched by electron based microscopy.

2.1.1 Scanning Electron Microscopy

A schematic of the main components of a modern SEM is shown in figure 2.1. The basic optical theory behind its operation shares many parallels with light microscopy.

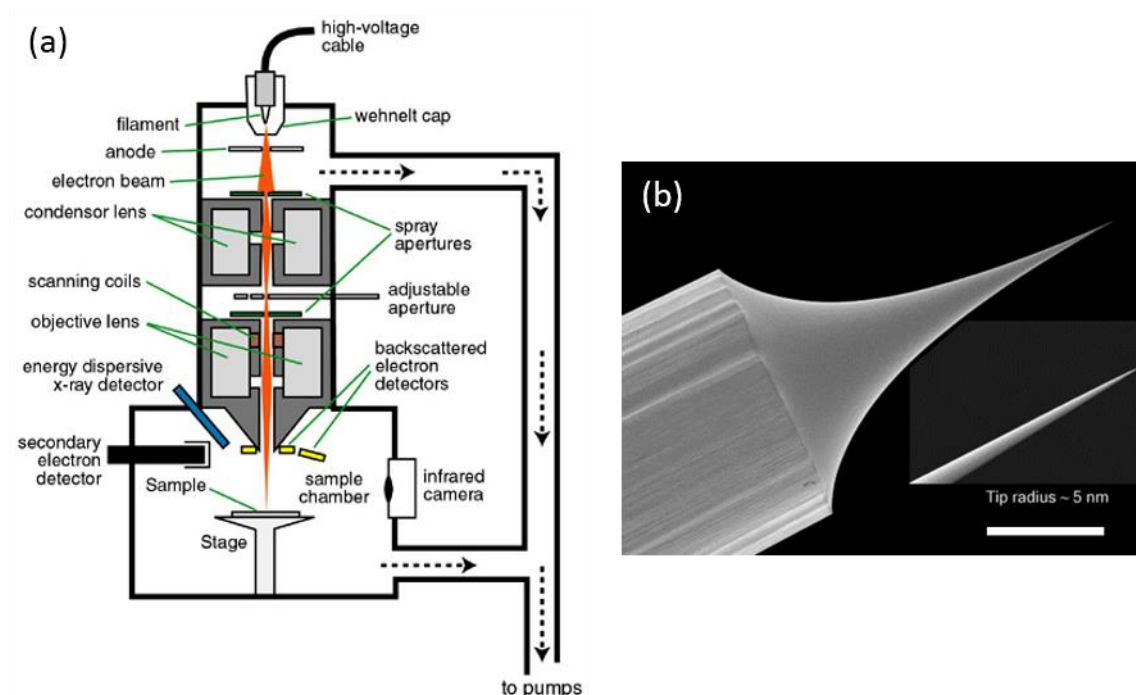


Figure 2.1. a) Schematic of the main components in a modern scanning electron microscope.⁴ b) High resolution SEM image of a tungsten <100> FE nanotip with 5nm radius; scale bar 100 μm.⁵

An electron ‘gun’ consisting of an extremely sharp conductive tip at the top of the chamber is placed at high negative bias relative to an annular anode further down the chamber and acts as the source of the electron beam. Multiple tip constructions are commercially available, each with their own merits and disadvantages. All SEM work described in this report was performed on a Zeiss Ultra SEM which utilises a Schottky emitter field emission gun (SE-FEG). This type of gun contains a filament source consisting of a tungsten (100) nanotip coated in a monatomic layer of ZrO_2 which has the effect of significantly lowering the work function of the tungsten tip⁶. A SE-FEG offers marked advantages over other source types, most notably a narrower beam size, lower maintenance requirements and brightness three orders of magnitude higher than those offered by alternative sources. A bright source is desirable as brightness is directly correlated to image resolution and the signal to noise ratio.³

Further down the column, the electron beam passes through a series of physical apertures and electromagnetic lenses which first collimate the beam into a parallel arrangement which can then be focussed by the objective lens. As in the case of light

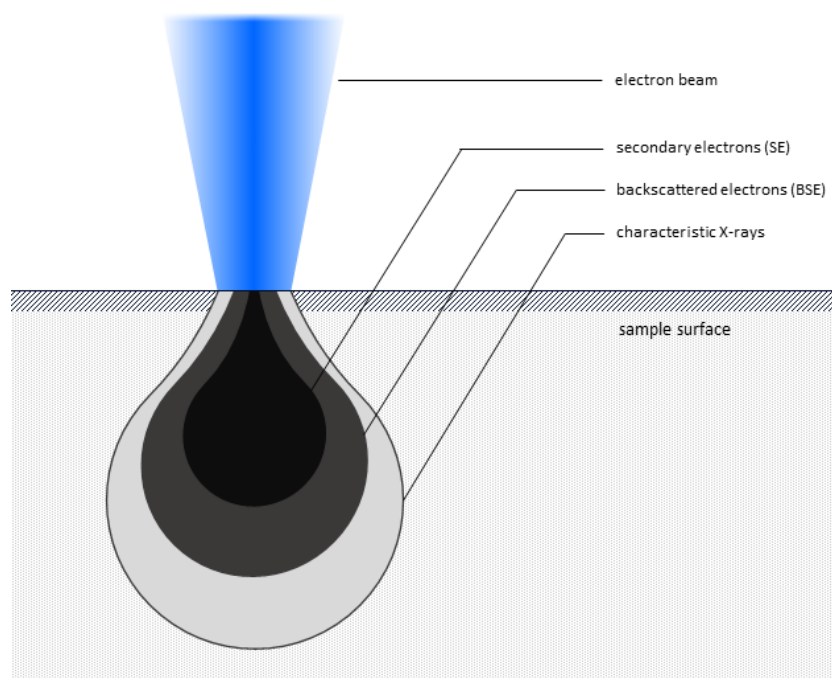


Figure 2.2. Summary of signals generated from the electron beam-surface interaction.

microscopy, the aperture size can be varied to modify the beam width with the effect of altering depth of focus in the final image. The larger the aperture used, the narrower depth of field in the final image. A set of scanning coils rasters the beam across the surface of the sample and signals generated from the resultant interactions are measured by an array of detectors in proximity to the sample.

Multiple types of interactions take place between the electron beam and the sample surface resulting in the graduated pear shaped excitation volume shown in Figure 2.2 which demonstrates the surface sensitivity of each type of signal. Several detectors are utilised in SEM imaging to capture and interpret each distinct signal type resulting in multiple imaging modes each containing different information about the sample. The most surface sensitive signal arises from emitted secondary electrons (SE) which originate through inelastic collisions between the electron beam and outer shell electrons of the sample atoms. Over 90% of SEs have energies less than 10 eV so only those formed within a shallow escape distance beneath the surface are able to reach the detector. Typically this escape distance is on the order of 5-10

nm and so images composed from SE signals contain extensive topographical information.⁷

Elastic scattering events occur when the incident electrons are strongly deflected by the nuclei of the sample atoms; the electrons lose a negligible amount of energy and are scattered at high angles. Electrons which are scattered at angles greater than 90° relative to the beam incidence are called back scattered electrons (BSE). The generation of BSEs shows a high dependence on the atomic number of the sample atoms and so contrast in a BSE image arises between areas of differing elemental composition.

2.1.2 Energy Dispersive X-Ray Spectroscopy

In addition to SE and BSE, the interactions between the high energy electron beam and a sample produce two distinct types of x-ray emissions. The first type appears as a low intensity continuous distribution of wavelengths which is visible as the low keV baseline noise in Figure 2.3 (b). This is known as Bremsstrahlung radiation and it arises from inelastic deflection events caused by interactions between the beam and charged particles in the sample.⁸

The second type of x-ray emission is produced when core electrons are ejected through inelastic collision, the 'hole' is then filled by an electron of higher energy and the excess energy is emitted in the form of a photon as shown in Figure 2.3 (a). These x-ray emission events produce intense peaks at a discrete set of wavelengths characteristic for individual shell transitions for each element. The process of identifying elements through their characteristic x-ray formation is called energy dispersive x-ray spectroscopy (EDX). The naming convention used in this technique is so that a K-shell hole filled by an electron from the L-shell results in a $K\alpha$ line signal on the spectrum. Comparing the obtained spectrum to reference values allows for element identification within a sample. Due to the rastering nature of the electron beam, high resolution spatial maps can be built up of the element distribution pattern. As shown in Figure 2.2, the formation of the x-rays analysed in EDX takes

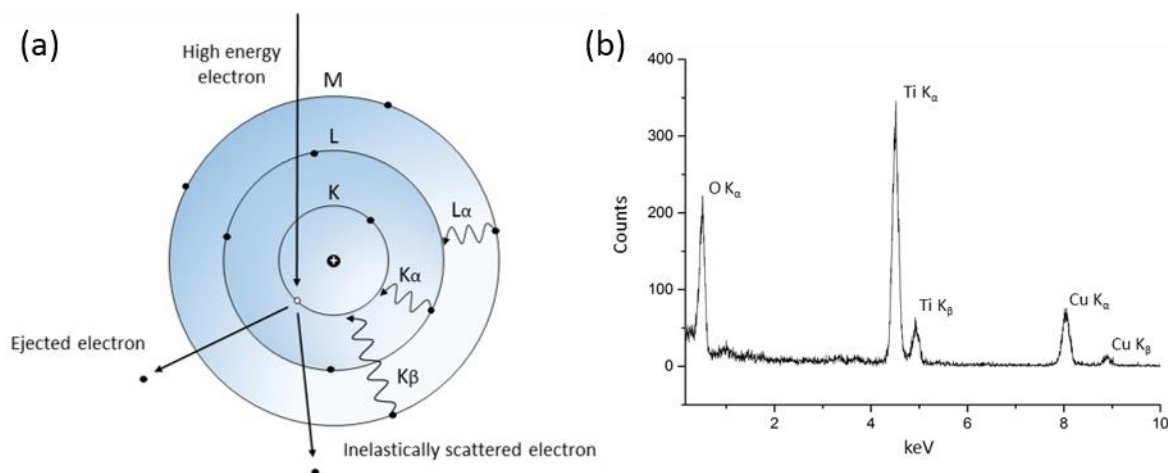


Figure 2.3. (a) Schematic of characteristic x-ray formation and (b) EDX spectra of TiO₂ nanowire on a copper TEM grid.

place in a deeper excitation volume than other signals resulting in reduced surface sensitivity. EDX can also be performed within a TEM allowing much higher energy transitions to be resolved and additionally the freestanding sample geometry required for TEM eliminates the issue of substrate signals dominating those of thin surface samples.

2.1.3 Transmission Electron Microscopy

The first electron microscope was a transmission electron microscope (TEM) constructed by Knoll and Ruska⁹ in 1931. While the dream of atomic resolution was not yet realised by this prototype, their pioneering work paved the way for the development of the field of electron microscopy. The operating principle of a TEM differs somewhat from that of a SEM. In TEM, electrons are accelerated at extremely high voltage (100 kV to 300 kV) toward a thin sample and the transmitted electrons are used to compose the final image rather than backscattered and secondary electrons in the case of SEM. As signal generation is dependent on transmitted electrons, an important sample requirement in TEM is electron transparency which limits specimen thickness to usually no more than 100 nm. Electron transparency is a function of both atomic number and beam energy so higher accelerating voltages can be utilised for thicker samples however this increases the risk of beam damage to the specimen. Many nanomaterials can be dispersed into a liquid suspension and

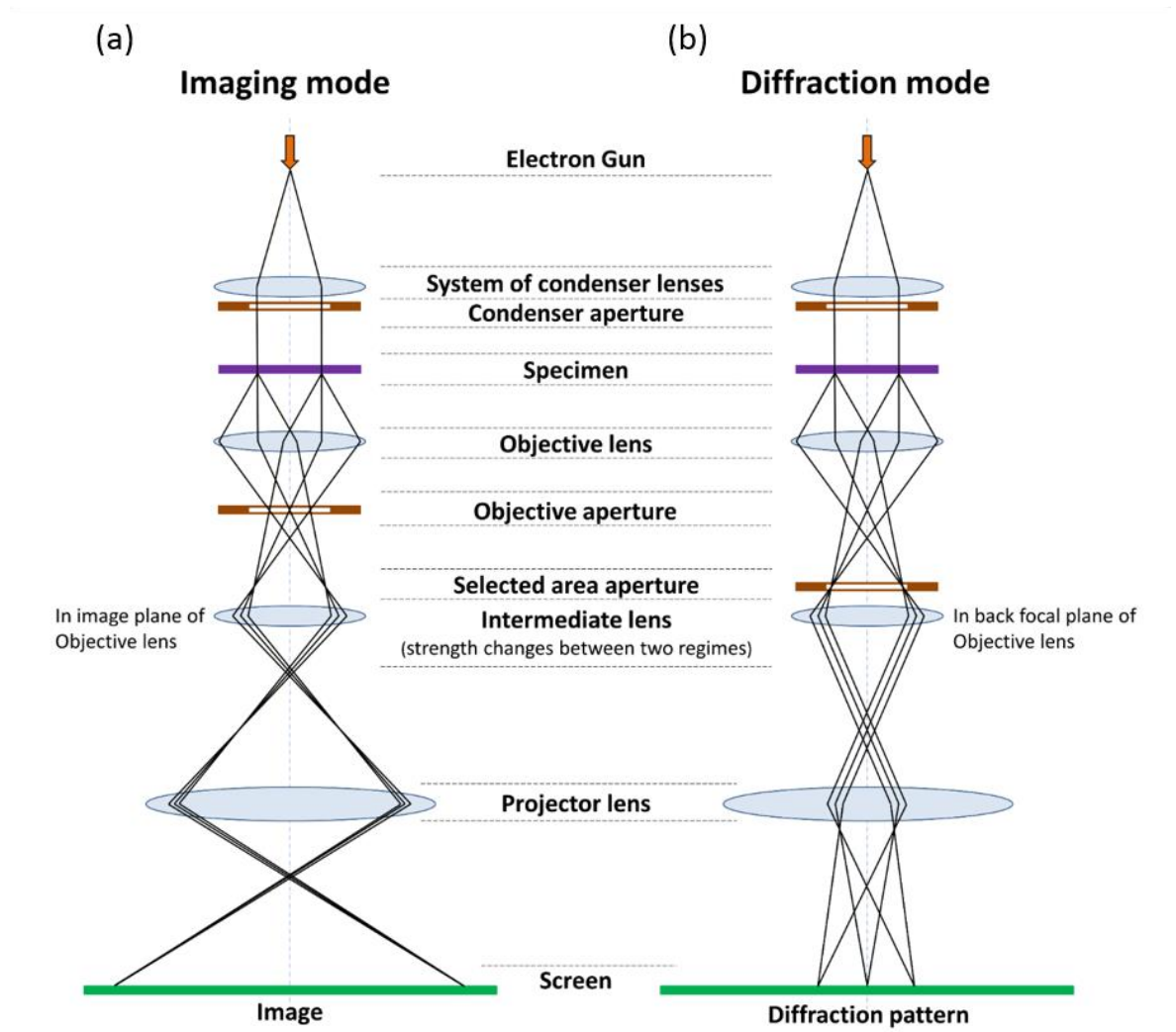


Figure 2.4. Schematic of TEM basic operating modes (a) standard imaging mode (b) diffraction imaging mode.¹⁰

then simply deposited onto a TEM grid. Bulk samples can also be examined using TEM once they have undergone an additional processing step known as lamella preparation. This technique involves a series of thinning operations utilising a focussed ion beam to mill away cross sections of the material until a suitable thickness is reached at the region of interest.

A TEM routinely uses much higher accelerating voltages than those of a SEM and accordingly is capable of significantly higher resolution. An accelerating voltage of 100 keV has a corresponding de Broglie wavelength of 4 pm and a theoretical Abbe resolution limit of 2 pm. While even higher accelerating voltages are available, it is

worth mentioning that in a TEM the actual limit of resolution is not set by the gun voltage but rather by the quality of the electromagnetic lenses and their ability to collimate and focus the electron beam. High resolution TEM (HR-TEM) can routinely achieve sub nanometre resolution allowing imaging of crystal planes and atomic resolution.¹¹

Figure 2.4 shows the main features in a standard TEM column and their configuration in both diffraction and imaging mode. Above the specimen lies the electron gun and various condenser lens used to focus and collimate the beam before contact with the specimen. The main differences between the two operating modes are the aperture selection and the strength of the intermediate lens. In diffraction mode, the SAD aperture allows the user to precisely control which region of the specimen contributes to the diffraction pattern. This has the advantage over standard x-ray diffraction of high selectivity over the region which contributes to the diffraction pattern, allowing investigation of crystallinity variation within a sample.

2.1.4 Atomic Force Microscopy

In order to characterise materials on the nanoscale, alternative technologies beyond the capabilities of standard light microscopy are required; the previously described techniques all rely on exploiting the wave-particle duality behaviour of electrons to produce an image. In many cases the operating conditions required for electron microscopy (high vacuum, sample conductivity, and resistance against beam damage) preclude the use of these techniques for characterisation. Atomic Force Microscopy (AFM) is a technique which uses an extremely fine nanoscale tip (50 - 0.5 nm) to physically map the surface topography of a sample.¹² It was developed in 1986 as a modification for a scanning tunnel microscopy (STM) system by Binnig *et al*¹³ and has since seen widespread adoption as a rapid and versatile imaging tool. Insulating surfaces can be imaged under ambient conditions unlike electron microscopes or STM. Additionally, as the image resolution is only limited by the sharpness of the tip, atomic resolution is readily achievable¹⁴.

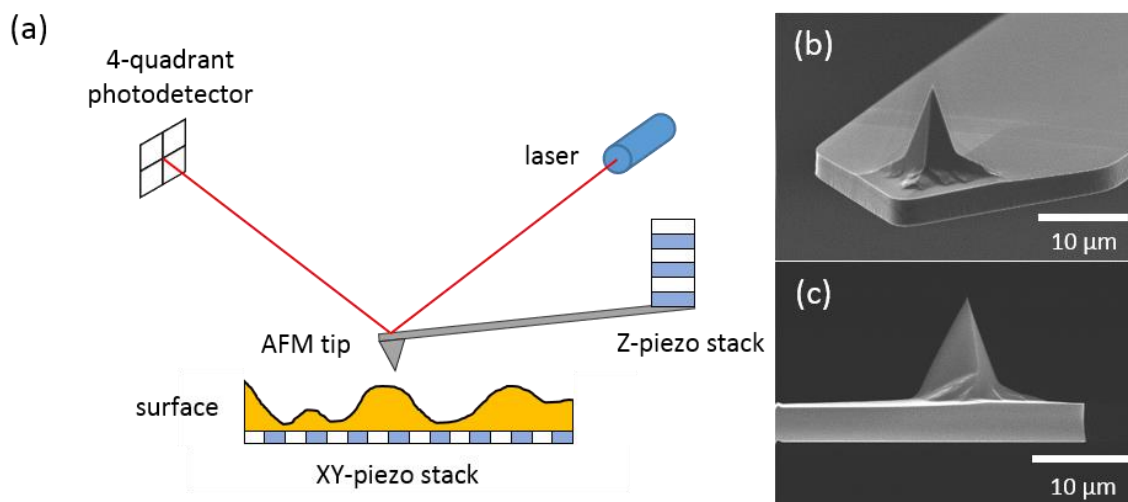


Figure 2.5. (a) Schematic of the basic components used during an AFM scan, the tip deflection is measured by the reflection of the laser off the back surface of the cantilever and onto the photodetector allowing a sample topography to be constructed. SEM images of cantilever with a silicon AFM tip from (b) an angled top down view and (c) a side view.¹⁵

The basic working principle behind modern AFMs involves a tip at the end of a cantilever being rastered across the sample while its interaction with the surface is monitored and controlled by a feedback loop. This setup allows for a three dimensional image of the surface topography to be constructed. The primary forces controlling the tip-surface interaction are typically Van der Waals or electrostatic depending on distance¹⁶, although specially designed tips allow for other interactions to be studied (e.g. electrical¹⁷⁻¹⁸, magnetic¹⁹ or thermal²⁰).

In the original AFM design an STM tip was placed in contact behind an AFM tip to monitor the tip deflection as it moved across an insulating sample¹³. In modern AFM setups, a laser beam is aligned onto the top surface of the cantilever and its reflection is focussed onto a four-quadrant photodetector (PD) as shown in figure 2.5. From the position of the reflected beam, both lateral and normal tip movements can be detected with extremely high precision allowing for picometer resolution. During rastering, each linescan records a 2D profile of the surface and over multiple scans a three dimensional topography of the sample surface can be constructed.

There are two main imaging modes in AFM, contact mode and tapping mode and each has their own merits and disadvantages. In contact mode the tip is approached to the sample surface and attractive Van der Waal forces cause the tip to 'snap' into contact. As the downward force on the tip continues to increase, the tip-surface interaction becomes repulsive as electrostatic forces become more dominant. It is in this repulsive regime, where the tip is applying a user defined set point force, that contact mode AFM is performed. The greater tip-sample interaction forces present in contact mode AFM yield improved signal to noise ratios than tapping mode AFM allowing for higher resolution imaging,²¹ however the applied normal force on the surface also produces a high lateral force which can lead to damage when imaging soft samples or movement of weakly adsorbed materials during scanning.²²

In tapping mode AFM, the tip is oscillated at its resonant frequency and lightly taps the surface building up a topography of the sample as it is rastered across. The oscillation amplitude of the tip is maintained at a constant user defined set point during scanning. As the tip approaches the surface, the amplitude of the oscillation changes due to the strongly distance dependant forces (Van der Waal, electrostatic) acting on the tip. The change in amplitude is monitored by the deflected laser on the photodetector and the Z-piezo shifts the tip position either closer or further away from the surface to return the amplitude to its original value. AFM has proven to be a versatile imaging tool and is capable of obtaining high resolution images on a wide variety of samples without the restrictive operating conditions required by other techniques such as STM or SEM.

2.2 Nanowire Network Fabrication

The aim of this work is to manufacture and investigate the electrical and optical properties of nanowire networks designed with continuous junctions. Two distinct patterning techniques are used in the fabrication of these networks and their underlying theoretical principles are discussed here. Additionally, both fabrication processes rely upon a plasma etching step during pattern transfer. The operating principles of the etching systems used are also detailed in this section.

2.2.1 Crack Lithography

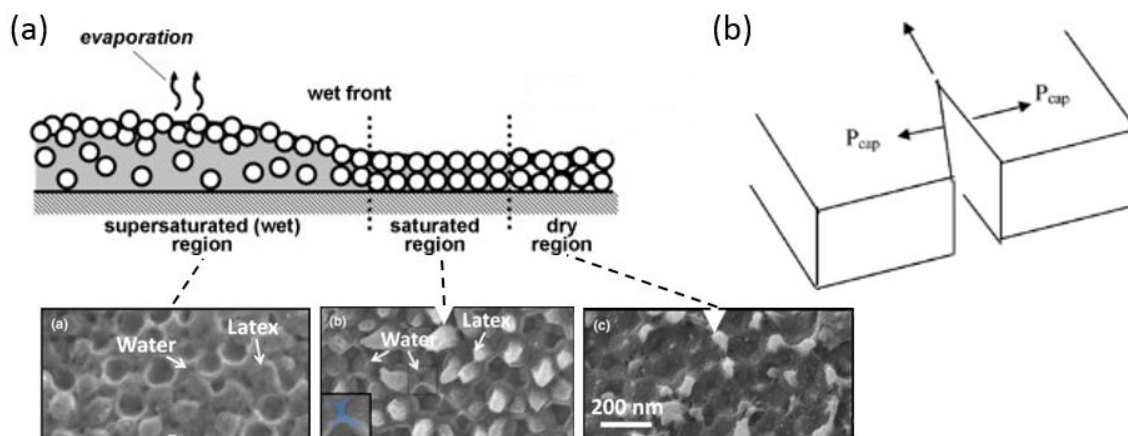


Figure 2.6. (a) Schematic of the different zones in the drying front of a latex particle film with accompanying environmental SEM images²³ (b) Schematic of a nucleated crack widening and elongating due to lateral capillary forces.²⁴

Crack lithography is a patterning technique which utilises the spontaneous formation of crack defects in colloidal films generated from solution. A colloid is a binary phase system consisting of discrete particles of one material dispersed within another material acting as an overall medium. Immiscibility between the two materials distinguishes a colloidal system from a homogenous solution. Several mixtures of material phases are possible, in the case of solid particles suspended within a liquid medium the colloid is known as a sol.²⁵ Some examples of sols include paints,²⁶ inks,²⁷ varnishes²⁸ as well as many other common suspensions.²⁹ The processing of sols into films across a substrate is a convenient strategy for the application of uniform coatings of solids and is used extensively in multiple industrial processes.³⁰⁻³⁴ A common observation during the drying of sol based films is the tendency for cracks to spontaneously generate across the surface and disrupt the homogeneity of the film. For the purposes of applying a continuous uniform coating of material this is an undesirable phenomenon. Additives,³⁵⁻³⁶ multistep coating techniques³⁷ as well as complex supercritical fluid based drying protocols³⁸ have been developed to prevent cracking.

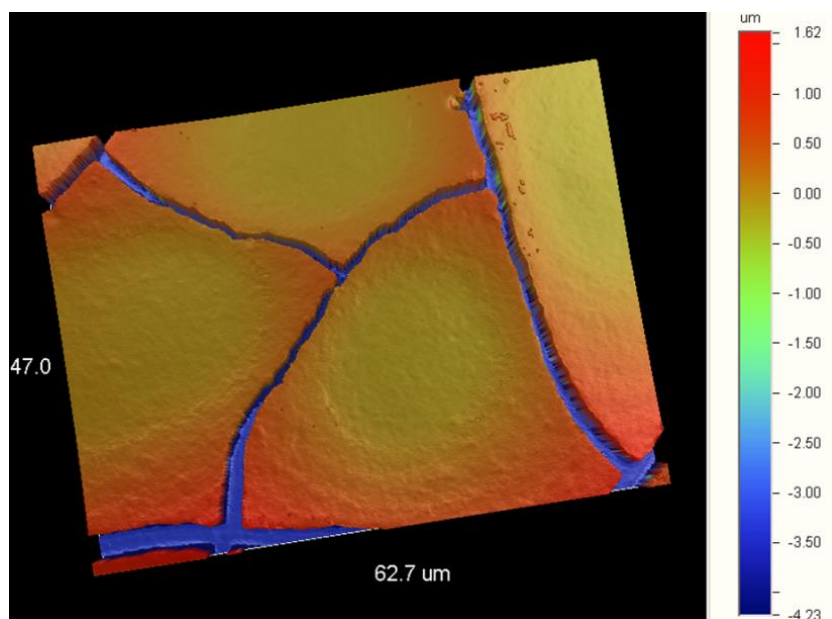


Figure 2.7. AFM 3D topography of an interconnected crack template formed from a film of acrylic nanoparticles.

In crack lithography, this natural phenomenon is exploited to produce an interconnected network of crack lines for use as a deposition template. Many models have been proposed to predict whether or not cracking behaviour, and to what extent, will be observed in a given film taking into account multiple factors such as the rigidity of the particles,³⁹ solvent-air interfacial tension,⁴⁰ particle-substrate adhesion⁴¹ and temperature and drying rate.⁴² A consensus on a complete quantitative theoretical model has yet to be reached, however it is generally accepted that capillary pressure from residual solvent acts as the main driving force behind the initiation and propagation of cracks in colloidal films.^{24, 43-45}

A film's tendency toward cracking originates from the reduction in volume that inherently takes place during the drying of a solid-liquid suspension. As shown in figure 2.6 (a), the removal of solvent decreases the interparticle distance until the particles are loosely packed together within a matrix of residual liquid in a saturated region. As evaporation continues, air begins to penetrate the film and the remaining pendular rings of liquid between neighbouring particles promote compressive capillary forces resulting in tensile stress in the plane of the film. In the case of soft particles this stress leads to deformation and fusion,³⁹ however with more rigid

particles, cracks spontaneously form across the film surface when the release of elastic energy during fracture exceeds the energetic cost of creating the new surface of the crack face.⁴⁶

The tensile stress a colloidal film experiences is directly proportional to its thickness,⁴⁷⁻⁴⁹ so following nucleation the film can either remain with isolated cracks or if sufficient residual tensile stresses exist in the film they may promote further elongation of the crack as shown in figure 2.6 (b). Crack lithography is performed in this high stress regime where cracks propagate from their point of nucleation and merge to form an interconnected void network amongst isolated film islands as shown in figure 2.7.

In this work, an acrylic nanoparticle based resin is used as a precursor solution to form crack templates which are then used as mask during metal deposition. The polymer based template allows for a clean lift off in organic solvent and the resultant metal mesh network is then used as an etch template in fabrication of a seamless silicon nanowire network. The full details of this pattern transfer process are detailed in chapter 3.

2.2.2 Electrospinning

Electrospinning is a technique for the fabrication of continuous fibres from a polymer solution drawn through a narrow tip at high voltage. This technique has garnered a great deal of attention in recent years in the field of nanomaterial synthesis for its scalability, range of available starting materials and potential fibre morphologies.⁵⁰⁻

⁵² In a basic electrospinning setup, a polymer solution is held in a reservoir and pumped at a constant user defined flow rate to form a hanging droplet at the spinneret tip. As shown in figure 2.8 (a), when a voltage is applied to the spinneret the droplet distorts to form a point called a Taylor cone⁵³ which stretches toward the grounded collector stage. At a certain critical voltage, repulsive coulombic forces overcome the surface tension of the droplet and a charged stream of fluid is emitted

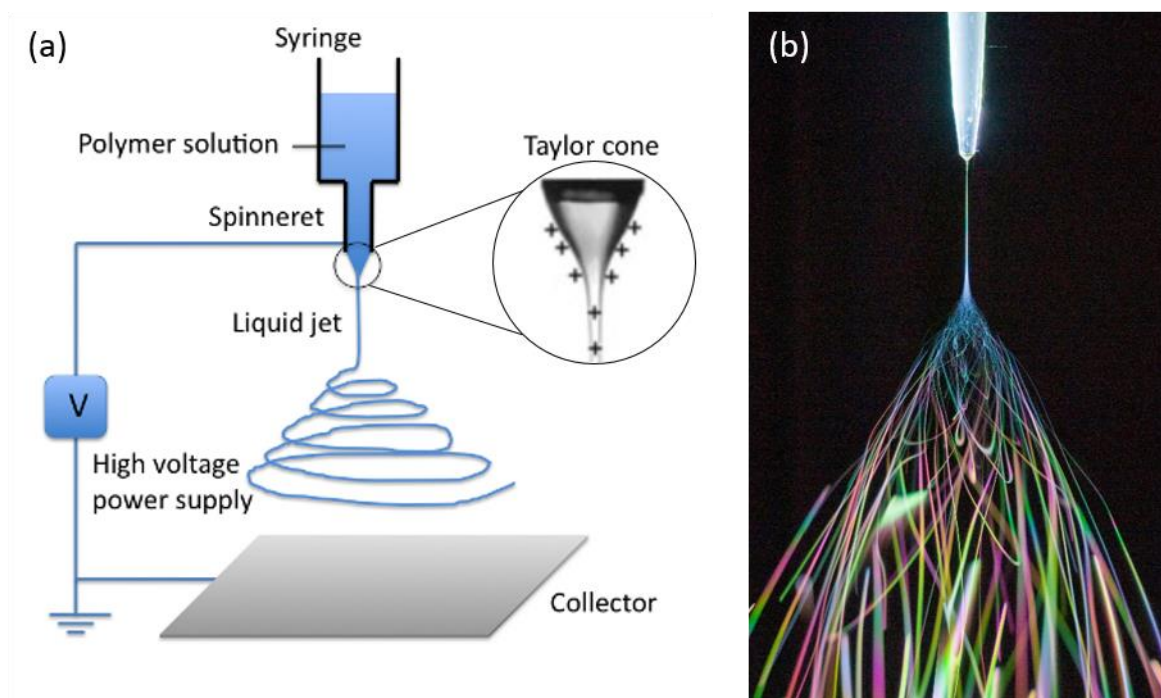


Figure 2.8. a) Schematic of a basic electrospinning setup⁵³ b) High speed photograph of the spinneret during electrospinning showing the Taylor cone and fibres undergoing whipping instabilities⁵⁴

from the tip of the Taylor cone. This fluid jet is continuously drawn and stretched as it travels from the tip toward the grounded collector. Initially the jet has a linear trajectory but after a short distance it undergoes a series of complex processes known as whipping instabilities⁵⁵ shown in figure 2.8 (b). The thinning of the liquid jet continues until evaporation of the solvent causes it to solidify and deposit on the collector as a dry fibre. This model based on electrostatic repulsion explains the electrospinning process qualitatively; however, in practice a large number of variables affect the morphology of the final fibres and extensive optimisation of multiple parameters is generally required.

As shown in figure 2.9, a plethora of fibre morphologies have been produced by tailoring the electrospinning process: smooth,⁵⁶ textured,⁵⁷ beaded,⁵⁸ tubular,⁵⁹ concentric⁶⁰ and segmented⁶¹ fibres as well as nanowebs⁶² and nanobelts⁶³ are some of the potential structures accessible through electrospinning. Many of these complex tubular structures are fabricated using specially designed spinneret heads⁶⁴ to simultaneously spin multiple polymer solutions. Virtually any polymer⁶⁵⁻⁷⁰ can be electrospun either through processing into a solution or through the use of a heated

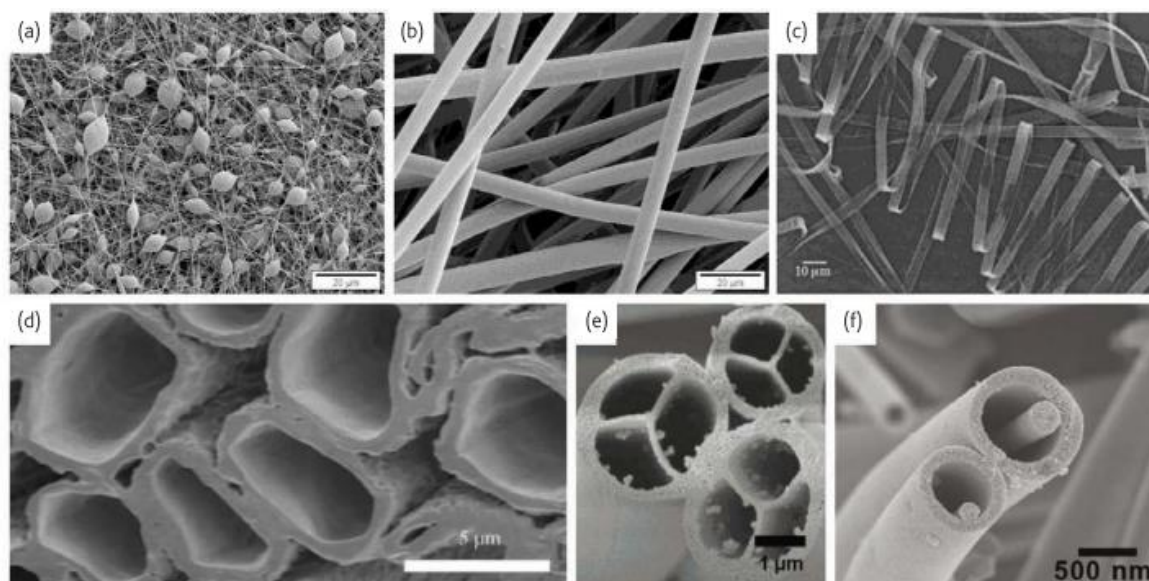


Figure 2.9. SEM images of a selection of the electrospun fibre morphologies from literature:⁷¹ (a) beaded, (b) smooth, (c) nanobelts, (d) single and (e) segmented tubular and (f) concentric fibres.

melt⁷² and many metal oxides⁷³⁻⁸⁰ have been processed into fibres using sol-gel solutions. The goal of this work is to fabricate smooth PMMA nanofibres with uniform diameters and investigate their potential as patterning templates, and so this discussion focusses on single polymer solution based electrospinning.

A large set of parameters exist which must be adjusted and optimised to produce a uniform fibre through electrospinning. Solubility of the polymer in a given solvent is obviously an essential requirement, however high solubility does not necessarily indicate a solvent system is suitable for use in electrospinning. For instance, PMMA is highly soluble in both toluene and chloroform but irregularly shaped particles⁸¹ or beaded fibres⁸² are the typically reported fibre morphologies using these solvents. Smooth, uniform diameter PMMA fibres have been fabricated using solvents in which PMMA is known to be less soluble,⁸³ such as THF⁸⁴ or DMF.⁸⁵ The higher dielectric constants of these solvents results in a more conductive fluid jet which experiences a more uniform distribution of coulombic charge, and therefore stretching forces, during electrospinning.⁸⁶ The conductivity of the solution can also be increased through the addition of salts which has been demonstrated to remove bead defects in fibres.⁶⁶

In addition to conductivity, viscosity of the polymer solution is known to have an important impact on the fibre morphology.⁸⁷ Solution viscosity is affected by the viscosity of the solvent to a minor extent but is primarily controlled by the molecular weight and concentration of the added polymer. At very low viscosities, electrospraying will occur instead of electrospinning and discrete particles will be formed rather than continuous fibres. In this low concentration regime, the chain entanglements between polymer particles are insufficient to stabilise the jet against the force of its own surface tension.⁸⁸ Rayleigh instabilities⁸⁹ overcome the coulombic repulsive forces and drive the fluid jet to minimise its surface area leading to it breaking up into isolated droplets.⁹⁰

Further increasing the solution viscosity, by either increasing the concentration of polymer or by using a higher molecular weight, typically produces ‘beads on a string’ or beaded fibres. In this regime Rayleigh instabilities still promote bead formation but stronger viscoelastic forces caused by the increased entanglement of the polymer chains prevent the complete breakup of the jet. Raising the solution viscosity further while keeping all other electrospinning parameters constant typically results in the formation of smooth uniform fibres. Beading caused by Rayleigh instabilities can also be prevented by the introduction of surfactants to reduce the surface tension of the solution.⁵⁸

Studies on other variables such as voltage,⁹¹⁻⁹² tip-stage distance⁹³⁻⁹⁴ and needle gauge⁹⁵⁻⁹⁸ have shown less consistent behaviour across differing polymer-solvent systems. Tendency toward bead formation and final fibre diameter are evidently influenced by a large number of interdependent factors. Experimental optimisation of these and other variables for a given polymer system continues to be the best strategy for controlling fibre morphology. Temperature and humidity have also been demonstrated to have a strong influence over the structure of the obtained fibres,^{68, 99-100} all electrospinning performed in this work was done in an ambient controlled laboratory at constant temperature and relative humidity (21°C, 50%). The electrospun fibres produced are used in a pattern transfer process exploiting the

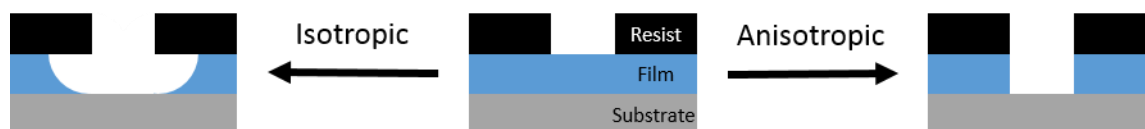


Figure 2.10. Diagram of trench profiles obtained from isotropic and anisotropic etching

orthogonal solubilities of PMMA and PS, the details of this templating technique and the optimisation of electrospinning parameters are described in full in chapter 4.

2.2.3 Plasma Etching

The methodologies employed for the fabrication of continuous nanowire networks in this work rely upon crack lithography and electrospinning for pattern formation. In both techniques, realisation of the final network structure depends upon selective plasma etching processes. A general explanation of the principles of etching will be described with reference toward the two types of plasma etching systems used in this work, a Diener Pico Oxygen Plasma System and an Oxford Instruments Plasma Lab System 100.

The selective removal of materials has become an essential tool in the manufacturing of semiconductor devices and can be achieved using either wet or dry etching processes. Lithographically patterned masks allow for selectivity over the areas where material will be removed and the edge definition between masked and exposed areas is dependent on the type of etch employed. Figure 2.10 shows the two ideal cases of the possible types of etch isotropy, a fully isotropic etch with an equal etch rate in all directions and an anisotropic etch with a vertical etch profile. In wet etching, solution based etchants are used to chemically remove material which typically results in uniform etching in all directions. Anisotropic profiles can be obtained from crystalline materials as in the case of silicon KOH etching, where different crystal planes display different reaction rates.¹⁰¹ Wet etching can offer near perfect etch selectivity, but extensive damage to nanostructures can occur as a result of capillary forces during the drying process.¹⁰²

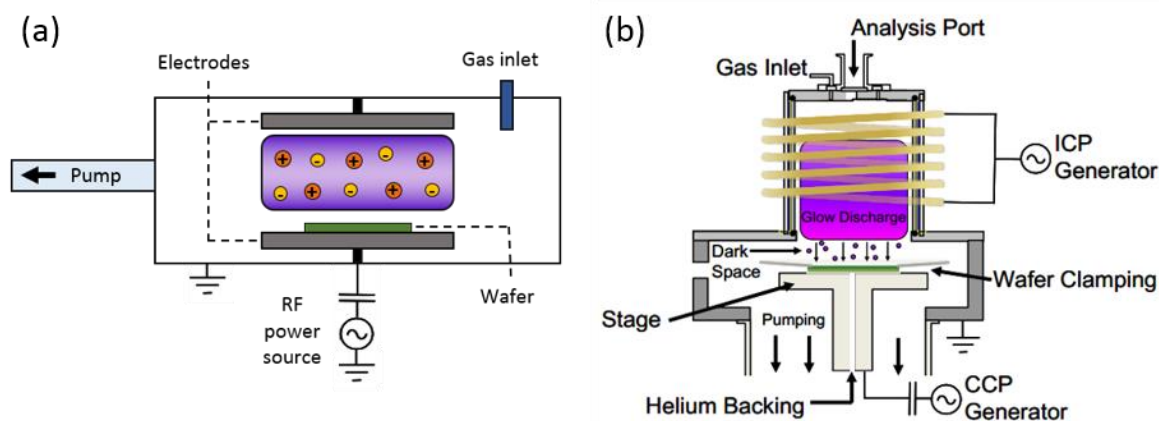


Figure 2.11. Schematic of (a) parallel plate plasma etcher and (b) a standard ICP etching system¹⁰³

In dry etching, a plasma is generated from a low pressure chamber gas and ions and radicals are formed and accelerated toward the sample. These highly reactive species may then collide against the exposed surface and form volatile products which are then removed from the chamber by a vacuum pump allowing further etching to proceed. Figure 2.11 (a) illustrates the setup of a typical parallel plate system. The plasma is generated through the application of a radio frequency electric field to the DC isolated wafer stage. With each cycle of this field, the electrons experience an acceleration toward and away from the stage while the much heavier ions cannot track with the high frequency of the field leading to ionisation. Further ion formation as well as the generation of radical species occurs as a result of collisions with gas molecules. As electrons collide with the sample stage a negative charge accumulates due to its DC isolation; this bias between the stage and the neutral plasma is responsible for accelerating the reactive ion species toward the sample and producing a directional etch profile.

In a parallel plate configuration, the RF signal applied to the wafer stage is responsible for both the generation of the plasma and the acceleration of the generated ions toward the sample, coupling together these parameters. In an ICP etching setup, as shown in figure 2.11 (b), plasma is generated inductively through a set of coils external to the gas chamber. Under the application of a RF signal the induced magnetic field accelerates electrons within the chamber resulting in collisions and the formation of ions. The design of this system allows the plasma

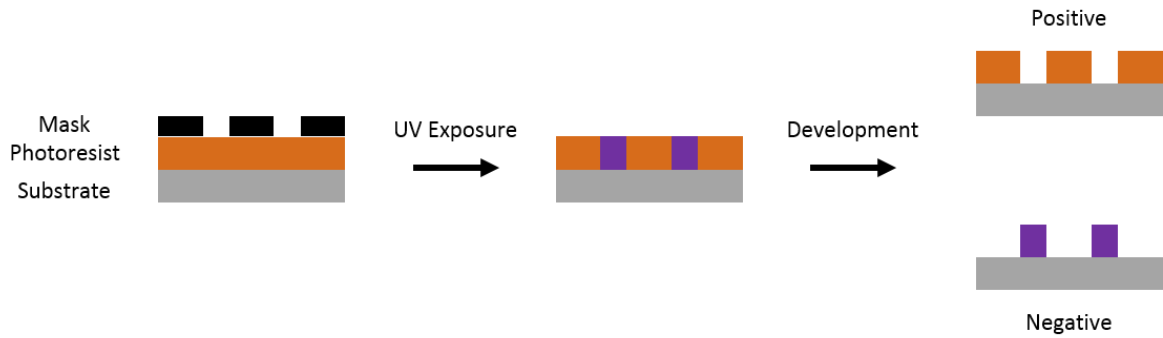


Figure 2.12. UV Lithography development process for a positive and a negative resist.

density to be controlled *via* the ICP power and a separate bias can be applied to the sample stage to control the momentum of the ions. ICP etching is widely used as it allows for fast etch rates and a high degree of control over the etch anisotropy.

2.3 Device Fabrication

Using the patterning techniques described in section 2.2, devices based off of both individual wires and larger scale networks are contacted and electrically interrogated. For larger network devices UV lithography is used to fabricate the contact pads over the network. In the case of individual nanowire based devices, mix and match lithography is used which utilises faster but lower resolution UV lithography for the alignment markers as well as slower but much higher resolution electron beam lithography for the contacts onto individual nanowires.

2.3.1 UV Lithography

The ability to pattern templates with high resolution features over a wide scale is a cornerstone of the microelectronics industry and the technique of UV lithography finds extensive use for this application. In this process, a solution of a photosensitive polymer known as a resist is coated onto a substrate and a mask is aligned and brought into contact with the surface. Masks are typically made from UV transparent borosilicate glass and patterned with a chromium film, the masked sample is exposed to a UV light source for a predetermined period of time which results in chemical modification within the exposed areas of the resist. There are two common types of photoresists available and they are distinguished by their behaviour under UV

1. Dehydration bake at 150°C for 5 min
2. Spin S1813 at 5000 rpm for 45 sec with 5 sec ramp at 500 rpm
3. Soft bake on hotplate at 115°C for 75 sec
4. Mask and expose with UV G-line source for 4-6 seconds
5. Develop in MF-319 for 45 sec and stop in H₂O for 30 sec

Table 2.1. UV Lithography recipe for S1813 positive photoresist.

exposure. Positive resists are rendered more susceptible to development following UV exposure and negative resists less so; the process steps for each of these resist types are illustrated in figure 2.12.

All UV lithography performed in this work was performed using Microposit S1813, a positive novolac-type resist supplied by Shipley. S1813 is a mixture of phenol formaldehyde (novolac) and diazonaphthoquinone (DNQ) and upon exposure to UV light an acidic compound is generated which significantly increases the film's solubility in the basic developer.¹⁰⁴ An OAL mask aligner was used for exposure and the exact lithography procedure employed in this work is detailed in table 2.1.

2.3.2 Electron Beam Lithography

The powerful imaging resolution of SEMs also facilitates the fabrication of complex nanoscale structures through electron beam lithography (EBL). EBL facilitates the production of intricate nanoscale features at improved resolutions compared to state of the art optical lithographic techniques.¹⁰⁵ EBL relies upon an electron sensitive polymer film called a resist which is deposited across the substrate by spin coating. The electron beam is rastered across the sample surface according to an arbitrarily user defined pattern in a modified SEM system installed with a beam blanker to prevent unwanted area exposure. As the polymer resist is irradiated by the beam, its chemical composition is altered resulting in either bond breaking for a positive tone resist or chain cross linking in the case of a negative resist.

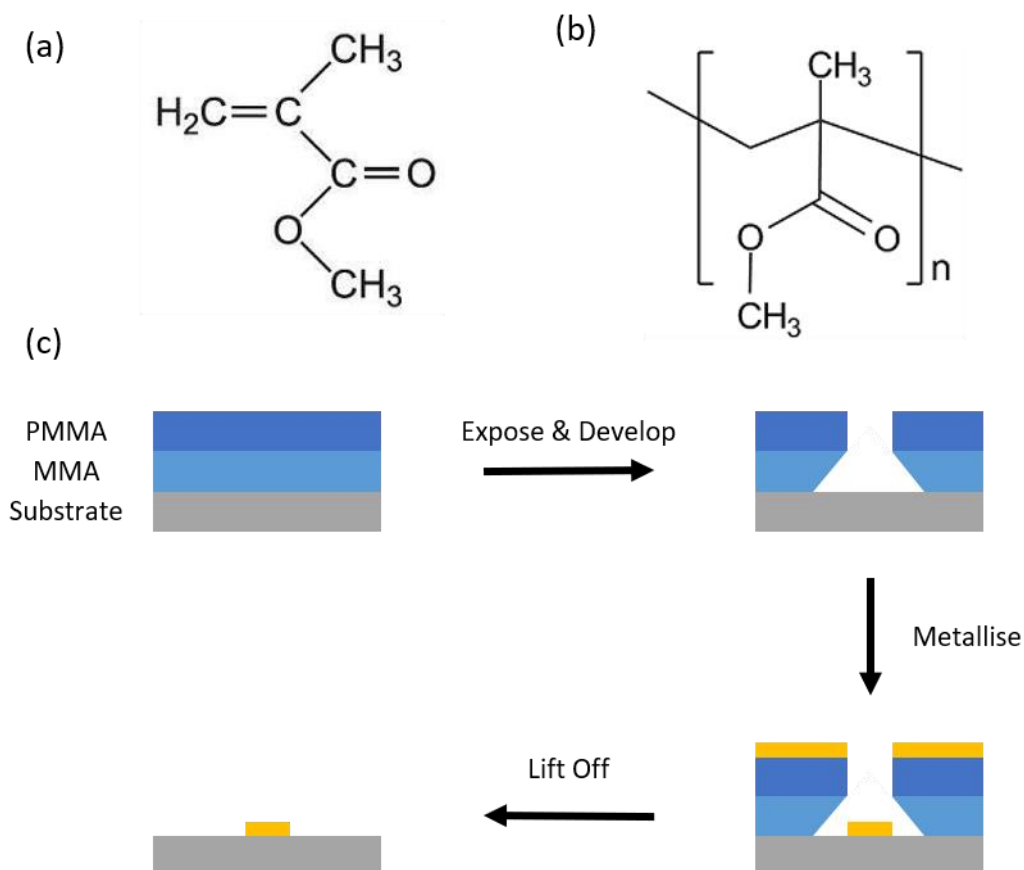


Figure 2.13. Molecular structures of (a) MMA and (b) PMMA¹⁰⁶ (c) General schematic of the electron beam lithography process using a positive tone bilayer resist for metallisation templating.

Once a pre-defined clearing dose has been applied, a considerable difference in solubility exists between exposed and unexposed areas which can be then be exploited using an optimised developing process. Once developed, a metal film of lesser thickness than the polymer resist is uniformly deposited on the substrate. All metallisation in this work was performed using a Temescal FC-2000 e-beam evaporator. A final lift off step is then performed in acetone which selectively removes the remaining resist and the deposited metal over the selected areas to realise the final pattern. In a positive resist, as illustrated in Figure 2.13, the areas exposed to the electron beam are removed leaving the substrate exposed for metallisation and the inverse pattern is obtained in the case of a negative resist.

As shown in Figure 2.2, the electron beam produces secondary electrons that are emitted outside the beam spot size incident on the surface. This is known as the

1. Spincoat MMA EL9 at 6000 rpm with 5 sec ramp at 500 rpm
2. Soft bake on hotplate at 180°C for 120 sec
3. Spincoat PMMA A3 at 3000 rpm for 45 sec with 5 sec ramp at 500 rpm
4. Soft bake on hotplate at 180°C for 180 sec
5. Expose with following parameters:
 - Accelerating voltage 10 kV
 - Aperture size 20 μm
 - Clearing dose 120 $\mu\text{C cm}^{-2}$
6. Develop in MIBK:IPA 1:3 for 60 sec and stop in IPA for 30 sec

Table 1.2. Electron beam lithography recipe for a bilayer resist.

proximity effect and it shows high dependence on both the beam energy and on the molecular composition of the resist¹⁰⁷. In this work, a bilayer resist is used which employs a film of PMMA overlaying a layer of lower density MMA. The MMA is more sensitive to beam induced chain cleavage and so a wider area is exposed relative to the overlying PMMA layer. This undercut feature profile is ideal for metal deposition as it avoids any contact between the material deposited on the substrate thereby preventing any disturbance to the pattern during lift off. All EBL in this work was performed on a Zeiss SUPRA SEM and patterns were designed with Raith Elphy Multibeam software. The procedure used for the bilayer resist used in this work is detailed in table 2.2.

2.4 Electrical Characterisation

This section discusses the techniques used for DC electrical characterisation of samples in this work. All electrical measurements were performed using a Keithley 4200 Semiconductor Characterisation System (SCS) which is a fully integrated unit containing a PC running Keithley proprietary software to operate the four Source Measure Units (SMUs). This system was connected to a Karl Suss PM-8 probe station

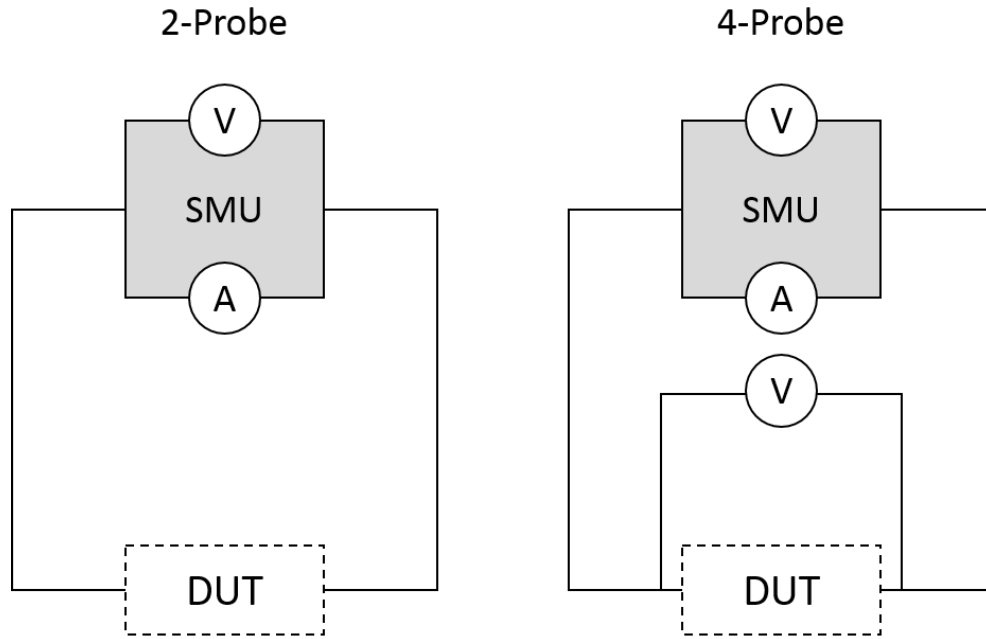


Figure 2.14. Equivalent circuits for 2 and 4 probe resistance measurements.

with low noise triaxial cables and the sensitivity limit of this setup was determined to be on the order of 10 fA at the highest amplification setting. The probe station contains an XY-translation stage and four micro positioners with tungsten needles allowing for accurate positioning and low pressure contact onto samples.

Resistance measurements can be performed using either a 2 probe or a 4 probe configuration as illustrated in figure 2.14. In a 2 probe setup, a single SMU drives a voltage across a device under test (DUT) and measures the current allowing for a resistance value to be calculated. This technique can produce accurate results when measuring high impedance samples, however the lead resistance and contact resistance between the probes and the contact pads must be taken into account when working with low resistance samples.¹⁰⁸⁻¹⁰⁹ This is accomplished in a 4 probe geometry by sourcing current between the outer two contacts and measuring the corresponding voltage drop across the DUT. The contact resistance can be effectively removed and an exact sample resistance value determined; the resistivity of the material may then be calculated through equation (7), where: ρ = resistivity, R = resistance, A = Cross sectional area and d = the distance between the inner edges of the inner contacts.

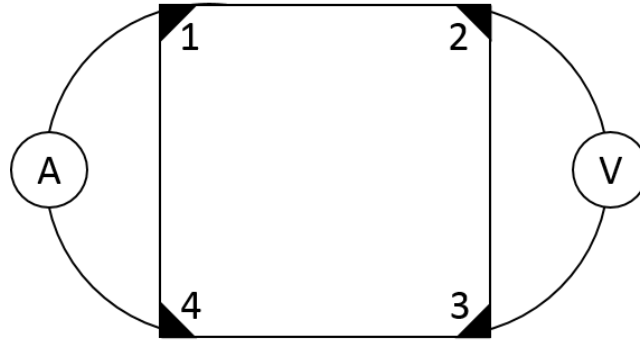


Figure 2.15. Van der Pauw probe setup for a square sample geometry.

$$\rho = \frac{RA}{d} \quad (7)$$

The Van der Pauw technique is another method for accurately measuring the resistivity of films and was developed from theory by Leo van der Pauw in 1958.¹¹⁰ The theorem describes a general strategy to accurately determine the resistance of an arbitrarily shaped sample which remains valid as long as a number of criteria are satisfied. The sample must have a flat shape of uniform thickness, be homogenous and isotropic and not have any isolated holes. The contact pad area must also be as small as possible compared to the size of the sample and all four contacts must be placed at the edge of the sample.¹¹¹ In the case of a square sample, Van der Pauw's theorem states that the equation for resistivity takes the form of equation (8).¹¹² For the contact setup shown in figure 2.15, the sample resistivity may be calculated using equation (7) where: ρ = resistivity, t = thickness, V_{23} = voltage measured across pads 2 and 3, and I_{14} = current sourced between pads 1 and 4.

$$\rho = \frac{\pi t}{\ln 2} \left(\frac{V_{23}}{I_{14}} \right) \quad (8)$$

The contact geometry was rotated clockwise around the sample and the measurement was repeated to allow an average resistivity value to be calculated.

2.5 Conclusion

In this chapter, the working principles of the many characterisation and fabrication techniques used in this thesis have been described in detail, both probe and electron based microscopy have been used extensively throughout this work for the analysis of nanoscale materials. The results chapters which follow describe in detail the application of crack lithography and pattern transfer processes using electrospun nanofibres toward the fabrication of interconnected nanowire networks with continuous junctions. Methods such as UV lithography and EBL have been described for the contacting of nanostructures and the techniques employed for electrical characterisation have also been detailed.

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3

Crack Templated Silicon Nanowire Networks

This thesis aims to explore new fabrication strategies for nanowire networks with seamless junctions and their potential applications for transparent and flexible electronics. In networks of individual nanowires the geometry at the junction interface acts as a highly resistive component in the device circuit and the overall performance suffers as a result. This chapter details the fabrication of silicon nanowire networks with seamless junctions and investigates their performance as transparent and flexible photodetector devices. The network fabrication process is detailed starting from a single crystal silicon on insulator wafer and a colloidal film crack templating technique is described. A metal assisted chemical etching process is introduced which forms discrete regions of porous silicon in the single crystal network. The effects of this structural modification on the devices photovoltaic behaviour are investigated and a proposed photoconduction mechanism is discussed.

3.1 Introduction

One dimensional systems such as nanowires and nanotubes have been the focus of a great deal of research interest over the last number of decades. Their unique structural, optical and electrical properties have made them attractive for multiple applications such as sensing devices,¹ medical drug delivery,² energy harvesting³ and storage⁴ technologies as well as others.⁵⁻⁶ A wide variety of synthesis techniques (e.g. polyol-reduction,⁷ vapour-liquid-solid (VLS) growth,⁸ surface energy driven growth (SEDG),⁹ template deposition¹⁰) have been developed and optimised such that the nanostructure morphology¹¹⁻¹³ and material composition¹⁴⁻¹⁶ can be now controlled with high precision by tailoring the process conditions. In the field of sensing technologies, many devices based on individual nanowires have been published and

have demonstrated high performance in terms of their sensitivity, response times and extremely small device footprint.¹⁷⁻²⁴ However, the task of reliably and reproducibly making electrical contact to a single 1D nanostructure remains an important issue preventing the implementation of such devices on a commercial scale. The extremely high resolution required for the fabrication of these devices necessitates tedious and costly electron beam lithography alignment and patterning steps which discourages the large scale adoption of these technologies.²⁵⁻²⁷

Networks assembled from randomly oriented nanowires have been investigated as more scalable alternatives to single nanowire based devices with a view to retain their desirable optical and electronic characteristics.²⁸⁻²⁹ The larger area of a network compared to a single nanowire eliminates the reliance on costly EBL based methods and contacting can be performed by techniques such as UV lithography that offer lower resolution but significantly higher throughput. The structure of a nanowire network lends itself extremely well for applications requiring transparency and flexibility. The behaviour of the network is determined by the particular nanowires used allowing for many possible device types to be constructed using this form factor. The optical transparency of the network is determined by the density of nanowires rather than their own optical properties, so a wide range of device functionalities can be achieved with this form factor while also allowing for high transparency to light.³⁰⁻

³⁴ Networks composed of nanowires made from a variety of materials have demonstrated stable performance during bending and strain tests and over many thousands of cycles.³⁵⁻³⁷ Additionally, the behaviour of a device constructed from a nanowire network will be based on the mean properties of the population of nanowires used. This allows for the inherent variations between individual nanowires to be averaged out which in turn leads to more predictable device behaviour.

Unfortunately, network based sensing devices do not typically perform as well as devices based on individual nanowires.³⁸⁻³⁹ This difference is primarily due to the junctions between intersecting nanowires present in the network. The minimal overlap geometry at the junction interface results in the introduction of an additional

resistive element in the device circuit that is not present in single nanowire devices. Additionally, the passivation layer coating the surface of the nanowires, which are necessary to prevent cold welding,⁴⁰ are typically composed of polymers⁴¹ or oxides⁴² with poor conductivity, further adding to the resistance of the nanowire junction interface. This junction resistance has been measured for a number of nanowire systems and has been proven to contribute significantly to the overall device resistance.⁴³⁻⁴⁴

In order to maximise the performance of a nanowire network based sensing device it is therefore essential to minimise the impact of junctions on the electrical behaviour of the device and so this work focusses on the development of seamless nanowire networks. In this chapter, the top down fabrication of silicon nanowire network with continuous in-plane junctions is described using a single crystal SOI wafer as a precursor. A colloidal film crack templating technique was employed to form a seamless metal network which was then used as an etch mask in a plasma etching process to transfer the interconnected wire pattern onto the underlying silicon device layer. A porous support film was patterned using a photoresist and was used to maintain the integrity of the network during the float transfer onto a transparent and flexible polyethylene terephthalate (PET) sheet. Following a series of chemical etches to remove the metal mask, the silicon network was subjected to a metal assisted chemical etch process (MACE) which introduced discrete sections of porous silicon into the crystalline network. The performance of the porosified silicon nanowire network as a transparent and flexible photodetector was investigated and mechanistic studies were carried out.

3.2 Results

In this section, the steps taken to fabricate the PET mounted silicon nanowire network mounted are each explained in detail following an overview of the process. A metal assisted chemical etching procedure is detailed which was used to introduce localised regions of porous silicon into the network structure. The performance of the porosified seamless silicon network as a transparent and flexible photodetector

was investigated and the results of low temperature mechanistic studies are explained in full.

3.2.1 Silicon Nanowire Network Fabrication

This section discusses the steps involved in the fabrication process of a Si NWN with seamless junctions from a SOI wafer precursor. The colloidal system used for the crack lithography patterning was studied and the relationship between the film thickness and the structure of the template was investigated. The anisotropy of the silicon plasma etch process used to transfer the topography of the crack templated Ti/Au network was imaged using angled SEM analysis. The effects of the chemical etches used to remove the metal etch template on the structure of the silicon network were investigated using passive voltage contrast SEM and quantified with image thresholding analysis. Finally, a float transfer procedure using a UV-resist based support structure was developed to mount the formed Si NWN on a transparent and flexible PET substrate.

3.2.1.1 Process Overview

A schematic overview of the procedure used to fabricate the PET mounted Si NWN is provided in figure 3.1. The SOI used in this work was a SmartCut™ fabricated SOITEC wafer with a 260 nm device layer (resistivity 1-5 Ω .cm) mounted on a 2 μ m thick BOX and was supplied by University Wafer. The first step of the process was the patterning of the SOI wafer through spin coating of a solution of acrylic nanoparticle resin and DI H₂O in a 1:1 volume ratio at 2000 rpm. This yielded a film with a thickness of 1.5 μ m which when dry resulted in isolated islands of film within a network of fully interconnected cracks. This cracked film was then used as a mask and 50 nm gold with a 10 nm titanium adhesion layer was deposited using ebeam PVD. A lift off step was carried out in chloroform overnight to remove the crack template leaving an interconnected metal network. An anisotropic SF₆/CHF₃ based plasma etch was then used to map down the seamless structure of the metal network pattern onto the underlying silicon device layer.

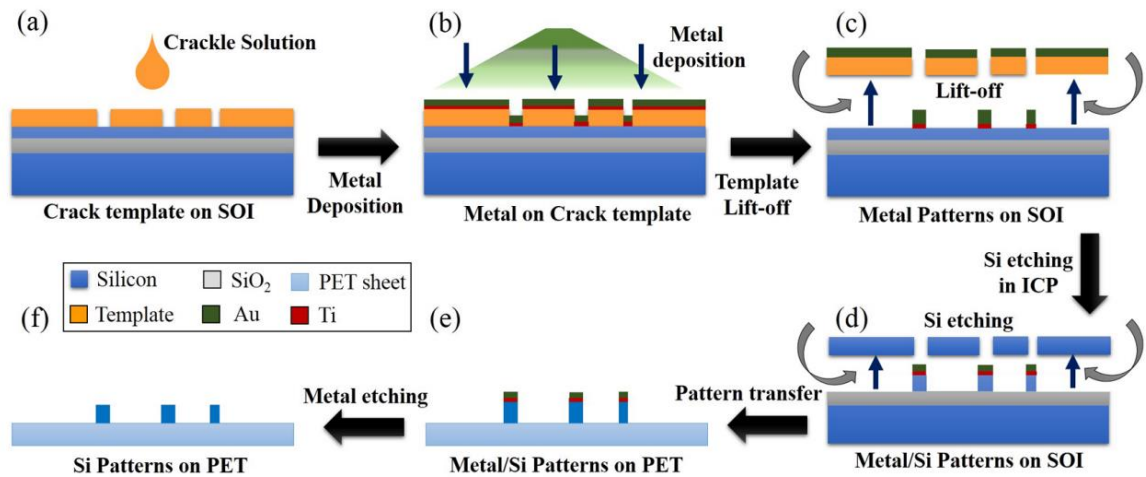


Figure 3.1. A generalised overview of the fabrication process for the PET mounted silicon nanowire network (a) formation of the crack template on SOI substrate (b) deposition of Ti/Au metal on templated SOI (c) acrylic crack template lift-off in chloroform (d) anisotropic ICP etching of silicon film masked with metal network (e) network transfer onto PET substrate and (f) etching of metal template.

To transfer the Si NWN from the oxide base to a PET substrate a float transfer procedure was developed. Firstly, a 1 μm thick layer of photoresist was patterned with 50 μm wide square openings regularly spaced at 50 μm separation. The patterned network was then placed in aqueous HF for 3 minutes to etch the oxide base layer.

The etched network was then lightly agitated at the surface of a 1:3 ethanol:H₂O solution until it separated from its substrate and was left floating. The network was then mounted onto a PET sheet by placing the sheet directly underneath the floating structure and slowly raising it out of the solution. The metal etch mask was retained during the transfer step to strengthen the network and help minimise fragmentation. After removal of the photoresist in acetone overnight, a series of chemical etches were performed using KI/I₂ and NH₄OH/H₂O₂ etchants to remove the gold and the titanium layers respectively. This yielded an interconnected silicon nanowire network mounted on a PET sheet; a final MACE porosification step was then performed which is detailed in section 3.2.3.

3.2.1.2 Crack Lithography

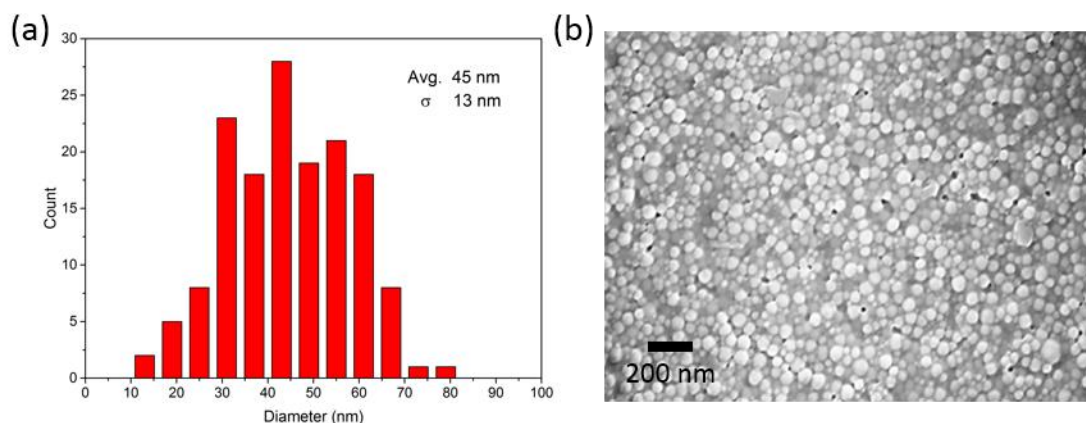


Figure 3.2. (a) Frequency distribution of diameters (measured from 152 particles) and (b) inlens SEM image of acrylic nanoparticles from resin solution.

As discussed in chapter 2, solution processed colloidal films often spontaneously crack across their surface due to induced tensile stresses from evaporation of residual solvent within the film. In coating applications this is typically an undesirable defect, however in crack lithography this natural phenomenon is exploited to create an interconnected network of crack openings for use as a deposition template.⁴⁵ The colloidal dispersion used in this work was an acrylic nanoparticle based resin supplied by Ming Ni Cosmetics Co., Guangzhou China. Figure 3.2 (a) shows a frequency distribution of nanoparticle diameters calculated from the SEM image of a spin coated film of these nanoparticles shown in figure 3.2 (b). The nanoparticles were found to be roughly spherical in shape with an average diameter of 45 ± 13 nm.

The supplied resin was first diluted with DI H₂O in a 1:1 volume ratio then stirred for 10 minutes and ultrasonicated for 30 minutes to break up any agglomerations of particles present. The dispersion was then centrifuged at 3000 rpm for 5 minutes and the supernatant was decanted off to remove any remaining undissolved large particles. This filtered solution was then spin coated on the SOI substrate at 2000 rpm for 120 seconds to give a film of 1.5 μ m thickness. This was determined to be above the critical film thickness where the induced tensile stresses are sufficiently strong to form an interconnected network of cracks as shown in figure 3.3 (d). For

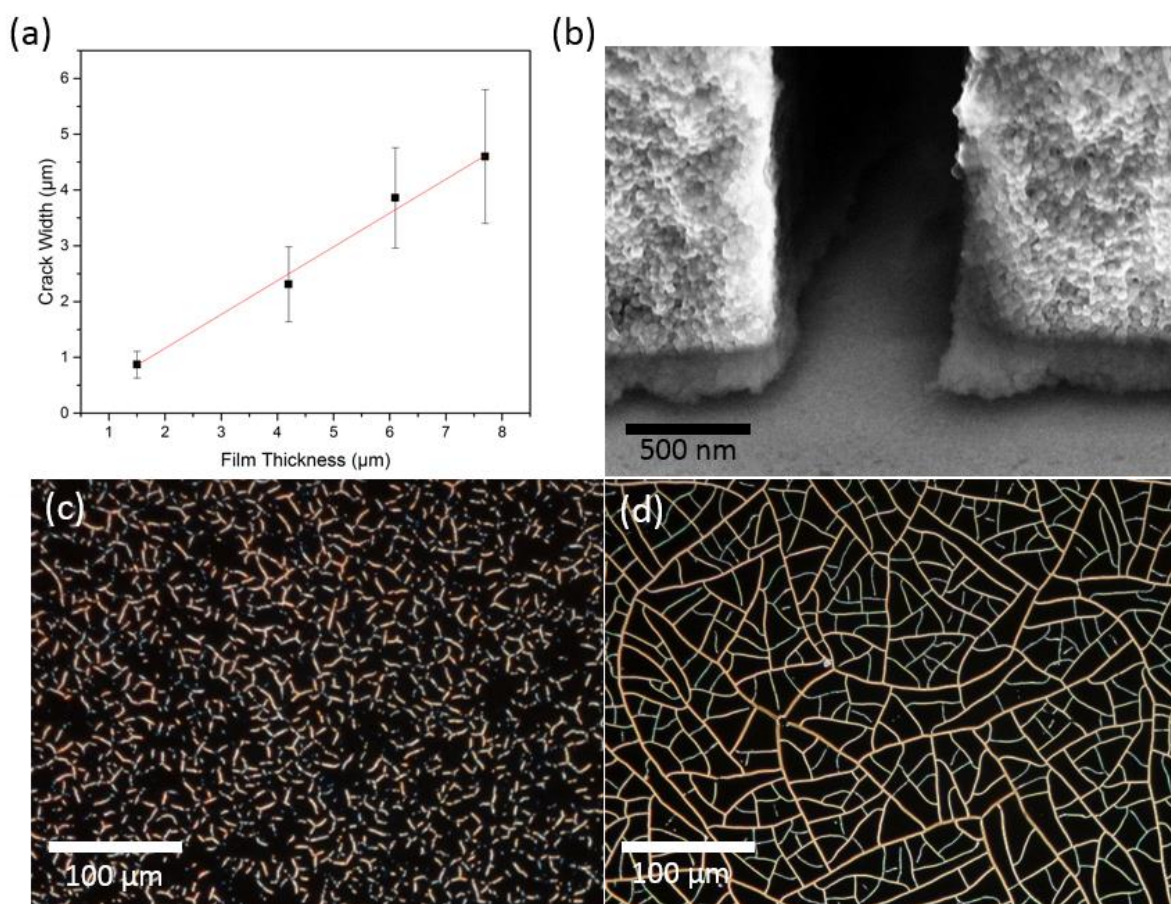


Figure 3.3. (a) Relationship between colloidal film thickness and average crack width (calculated from 25 measurements), (b) SEM image of crack edge profile from a 1.5 μm thick film, (c) Dark field optical image of colloidal film below critical thickness showing isolated cracks in film and (d) Dark field optical image of 1.5 μm thick crack template with a percolative void network.

films below this critical value, cracks were observed to nucleate across the film surface but did not merge to form an interconnected network. Cracks in thick films were found to penetrate the entire thickness of the film, figure 3.3 (b) shows an angled SEM image taken at the edge of a crack showing the exposed substrate layer below. Further increasing the film thickness leads to the formation of wider cracks, the relationship between average crack width and film thickness was determined to be linear as shown in figure 3.3 (a).

Figure 3.4 (a) shows a histogram of the crack widths measured from SEM imaging of a 1.5 μm thick film template. The average width was found to be 902 nm with a wide standard deviation of 236 nm. While smaller crack widths could be obtained by

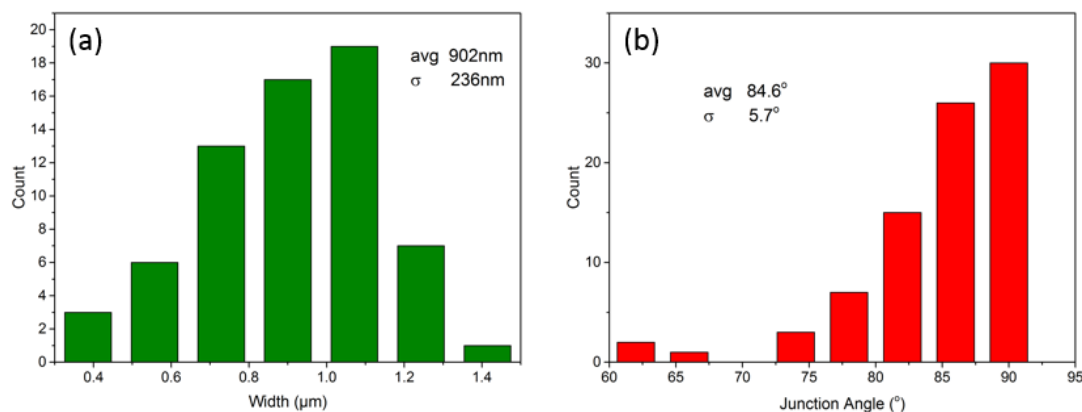


Figure 3.4. (a) Frequency distribution of crack widths (calculated from 70 measurements) and (b) acute angles between wire junctions (calculated from 80 measurements) from a 1.5 μm thick film.

using thinner films, growth of these cracks was halted shortly after nucleation and they did not merge together to form a connected network. This film thickness was used for all devices fabricated as it gave the narrowest percolative crack template that could be obtained using this particular colloidal system. During the drying process, the induced tensile film stresses are relieved through the nucleation and propagation of cracks. As the newly formed cracks spread and merge to form a network, the angle of intersection between wires was observed to approximate a right angle shown in figure 3.4. (b). Theory predicts that at the edge of the film, the compressive strain is only experienced in the direction parallel to the edge.⁴⁶ Therefore to provide the maximum relief of strain for the film, a new crack should propagate perpendicularly at the edge of an existing crack. Our observation of a junction angle distribution closely centred around 90° with a sharp tail is in agreement with this prediction.

3.2.1.3 Pattern Transfer and Network Morphology

Following the formation of a crack template on the SOI substrate, 50 nm Au was deposited with a 10 nm Ti adhesion layer using an ebeam deposition system. Several organic solvents (NMP, acetone and chloroform) commonly used in lift off processes were tested and of these, chloroform demonstrated the most successful template removal. Sample lift off was therefore carried out in chloroform overnight to remove

SF ₆ (SCCM)	80
CHF ₃ (SCCM)	13
Forward power (W)	1200
RF power (W)	22
Bias voltage (V)	83
Helium flow (SCCM)	6.1

Table 3.1. Plasma etching conditions used for SF₆/CHF₃ ICP silicon etching.

the polymer mask and extraneous metal to yield an interconnected network of metal nanowires matching the void pattern of the cracked film. This metal NWN was then used as an etch mask to transfer this interconnected network pattern onto the underlying silicon device layer. The plasma etching of silicon is widely used for industrial scale fabrication of microelectronics and the process chemistry is well documented.⁴⁷⁻⁴⁹ A SF₆/CHF₃ based ICP etch recipe was selected for use in this work; plasmas generated from this feed gas mixture contain highly reactive fluorine radicals which react with the silicon surface to form volatile species such as SiF₄.⁵⁰ The gaseous products are then removed from the process chamber by a vacuum pump.

The etching conditions used in this work are shown in table 1, the forward power controls the density of ions in the plasma while the RF power is responsible for acceleration of the generated ions toward the sample. The observed anisotropy is caused by the formation of a passivating fluoropolymer on exposed sidewalls which inhibits lateral etching. The directional bombardment of reactive ion species suppresses fluoropolymer growth on horizontal surfaces allowing for vertical etching. The sputtering effect of these ions also prevents the formation of ‘micrograss’ structures⁵¹ which are often observed during anisotropic etching.⁵² These optimised process conditions resulted in a near ideal anisotropy etch sidewall profile of 90.2° as shown in figure 3.5 (b) and the metal layer protected the masked silicon areas with no visible undercutting or delamination. An etch rate of 5 nm/s was measured

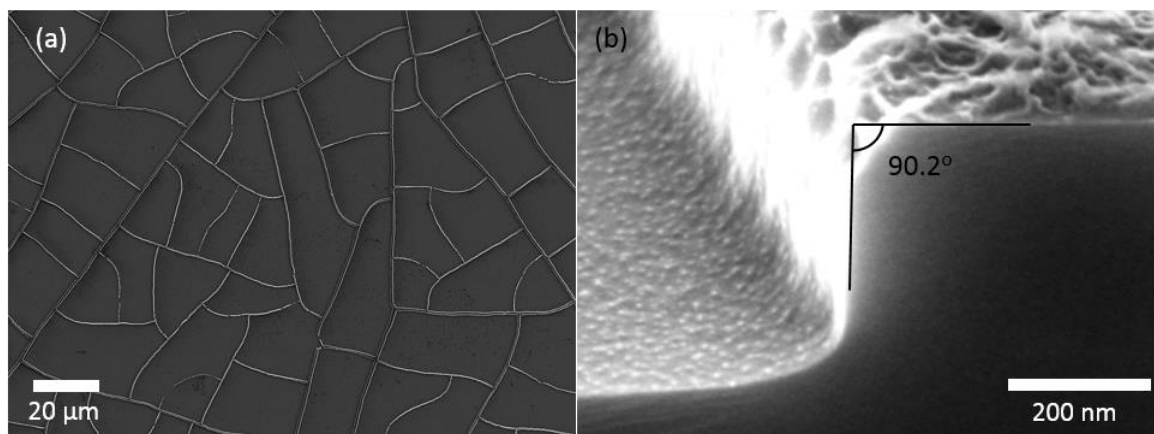


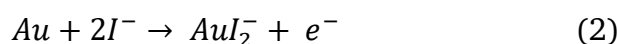
Figure 3.5. (a) Large scale SEM image of etched Si NWN with metal mask after plasma etching (b) High angle SEM image showing the sidewall profile of an etched Si NW.

and after a 60 second etch time, all unmasked regions of the 260 nm silicon film were cleanly removed down to the BOX layer as shown in figure 3.5 (a).

After plasma etching to form the Si NWN structure, the next step in the fabrication process is the removal of the Ti/Au etch mask. Gold is highly stable in most aqueous solutions and in order to induce dissolution it must be first oxidised and then complexed to form a soluble compound.⁵³ An aqueous solution of KI/I₂ was chosen to selectively remove the gold top layer, this etchant is widely used in industrial processes as a safer alternative to cyanide based etchants and its chemistry has been well documented.⁵⁴⁻⁵⁵ The etching mechanism works through oxidation of exposed gold metal by iodide anions forming a negatively charged diiodogold complex as shown in equation 2. Equation 3 details the corresponding reduction reaction which involves a triiodide species formed in the equilibrium reaction shown in equation 1. The overall balanced reaction scheme is shown in equation 4, the etchant solution used in this work was an aqueous KI/I₂ solution known as GE-8148 and was supplied by Transene. All samples were kept in solution for 5 minutes and then rinsed in DI H₂O to ensure total removal of all gold present.



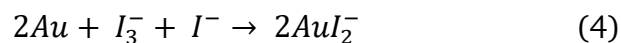
Anode:



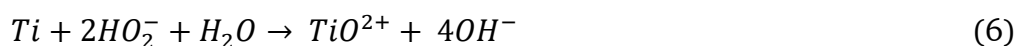
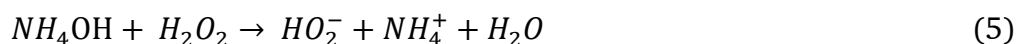
Cathode:



Overall:



A solution of 35% aqueous NH_4OH and 30% H_2O_2 in a 1:2 ratio was selected to remove the underlying 10 nm titanium adhesion layer. The chemistry of this etch relies upon the formation of the peroxide anion via deprotonation of H_2O_2 as shown in equation (5). This highly reactive species then oxidises the metallic titanium to form a tetravalent titanate as shown in equation (6). Once oxidised, this titanium species then readily forms a highly soluble peroxy titanate complex which is removed into solution exposing the underlying titanium for further etching. Equation (7) details this complexation, the reaction quotient of which has been reported to be on the order of 10^{12} so formation of the soluble product is highly favoured.⁵⁶ A secondary complexation reaction between the tetravalent titanate species and H_2O_2 also takes place as shown in equation (8), however this reaction has a significantly lower reaction quotient of $10^{3.7}$ so it does not significantly contribute to etching.⁵⁶ The overall primary reaction scheme for this titanium etching process is shown in equation (9). The reagents were mixed and left to stand until bubble formation could be observed, the samples were then placed in the solution for 2 minutes before being removed and thoroughly rinsed in DI H_2O .



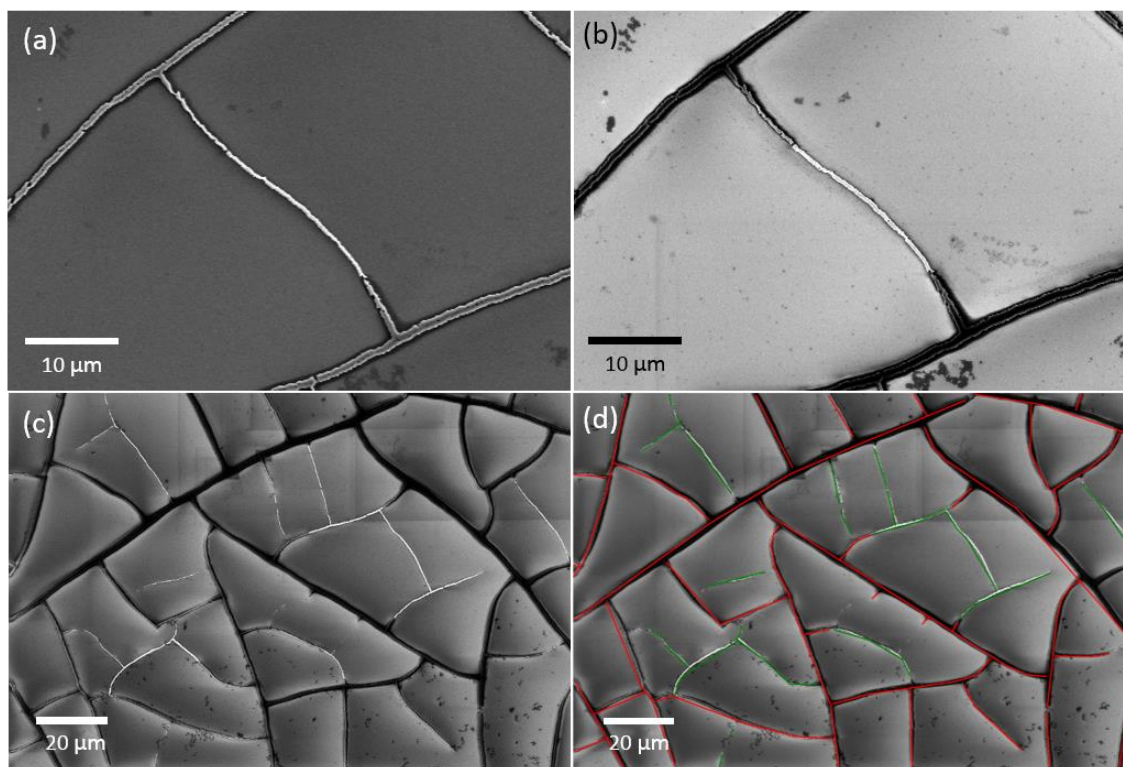


Figure 3.6. a) SEM image of a silicon NWN section mounted on $2\mu\text{m}$ SiO_2 taken with a SE2 detector b) The same section of network imaged using an inlens detector showing clear contrast between isolated central segment and the main network body c) Larger scale inlens contrast image of network d) Main network body highlighted in red and isolated sections in green.

The KI/I_2 etchant process is relatively mild and highly selective for gold removal, however the aggressive nature of the reagents used in the titanium etch result in a degree of damage to the underlying silicon network. The high solution pH accelerated the decomposition of hydrogen peroxide⁵⁷ and gaseous O_2 could be seen nucleating across the surface of the network during etching. Analysis of the silicon network structure showed a number of wire segments disconnected from the main body of the network. This could be visualised in SEM using a passive voltage contrast technique. During this process the network was grounded at the edge of the sample chip and the electron beam was focussed on a small area of the network. Throughout imaging, electrons incident from the beam are accelerated toward the sample and negative charge builds up on the network. This charge was able to be freely dissipated from sections which had a connection to ground. However, nanowires that were isolated from the grounded network accumulated a net negative charge as it was isolated on a thick insulating oxide layer. This excess charge increased the

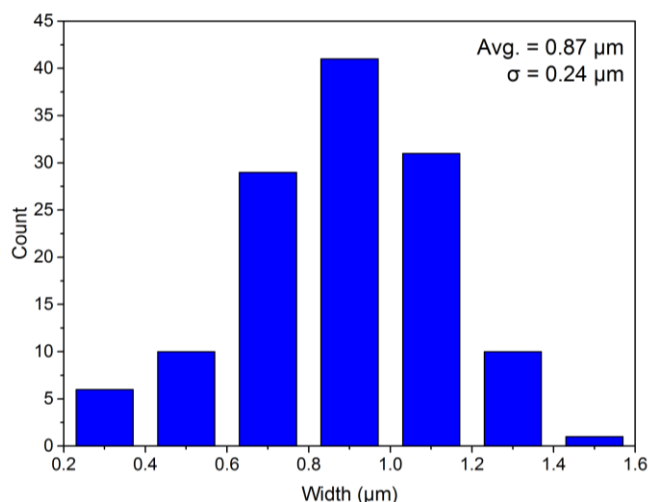


Figure 3.7. Frequency distribution of silicon nanowire widths (calculated from 140 measurements) after metal etching measured using SEM.

probability of SE emission relative to a neutral wire section producing contrast between connected and unconnected nanowires.⁵⁸

Figure 3.6 (a) and (b) show the same section of a Si NWN with an isolated central nanowire segment imaged with the SE2 and inlens detector respectively. The added contribution of BSEs to the generation of the SE2 image reduces the observed contrast compared to the inlens detector image which is composed entirely from secondary electrons. This technique allowed for the extent of fragmentation in the final Si NWN to be quantified. Figure 3.6 (c) shows a larger scale image of the network with the connected and unconnected section highlighted in (d). Image analysis performed over 10 images each of area $18,000 \mu\text{m}^2$ by our collaborators in the Ferreira group placed the percentage of the Si NWN that was isolated from the main network body at $33.4 \pm 6.2\%$.

Further image analysis of SEM micrographs provided additional information about the Si NWN morphology. The average fill factor of the network, the ratio of area covered by the network to the total area, was determined to be 12% and the average distance between wires was measured as $30 \mu\text{m}$. The average width of the final silicon nanowires was measured at $870 \pm 240 \text{ nm}$ as shown in figure 3.7. This closely matches with the original crack template average width of $902 \pm 236 \text{ nm}$.

3.2.2. Network Float Transfer Process

After etching, the silicon NWN is mounted on a 2 μm oxide layer upon a thick silicon wafer handle. In order to transfer the network onto a PET substrate, a float transfer process was developed using a photoresist mesh as a support. Firstly, a 1 μm thick layer of S1813 photoresist was coated over the network and patterned with 50 μm wide openings arranged in a simple square lattice formation as shown in figure 3.8. The patterned network was then placed in 10% (v/v) hydrofluoric acid for 3 minutes to etch away the underlying oxide layer. The openings in the photoresist mask facilitated a uniform etch rate of the oxide across the network; using an unpatterned photoresist layer as a support resulted in the network buckling inwards as etching could only occur at the edges of the film. Etch attempts without a photoresist support led to widespread breakage of the network into individual nanowire segments, even with the resist support this is a challenging process to perform and out of 5 attempted transfers only 2 were carried out successfully giving a process yield of 40%.

After the oxide layer had been etched away, the substrate was gently agitated at the surface of an ethanol and water mixture and the network separated and was freely suspended by the surface tension of the solution. Pure water, pure ethanol and several mixtures were tested, and a solution of 1 part water added to 3 parts ethanol by volume provided the ideal surface tension to allow for both floating of the supported network and successful transfer onto PET. The thick photoresist mesh helped to keep the network buoyant at the surface and also to maintain the structure of the network during transfer. To mount the Si NWN, a PET sheet was placed directly underneath it and gently raised out of solution at an angle to adhere the floating network to the PET substrate. The mounted network was then heated to 70°C for 5 minutes and left in acetone overnight to remove the photoresist support, the temperature was kept below 80°C to prevent cross linking within the photoresist support and a 5 minute annealing time was found to be sufficient to prevent delamination during lift off. Finally, the Si NWN/PET device was annealed at 70°C

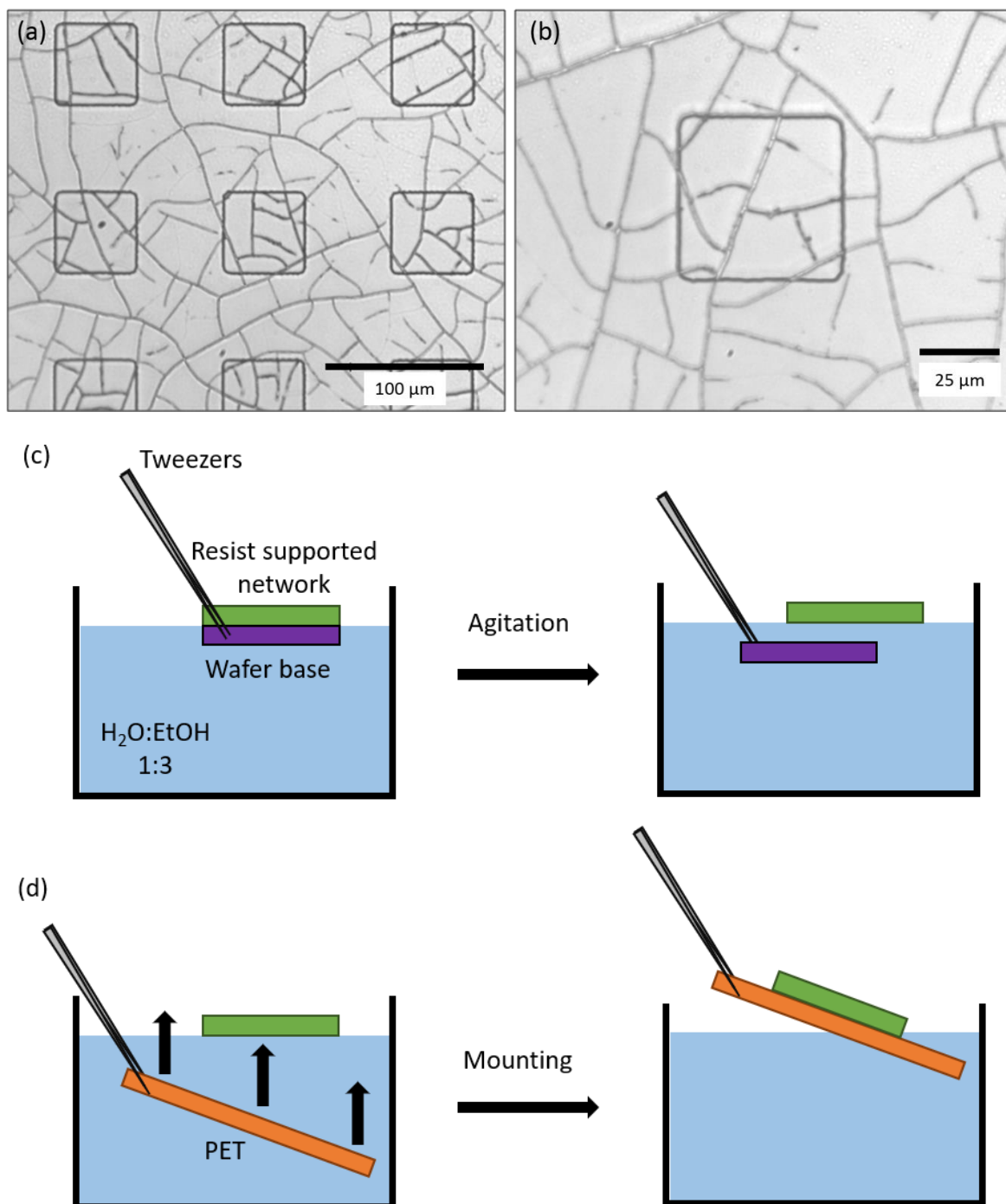


Figure 3.8. (a) Optical image of the 50μm pitch photoresist support mesh used during membrane transfer (b) Close up of an individual opening (c) Schematic of the first stage of the transfer process to float the supported nanowire network (d) Schematic of the final transfer step showing the angled PET sheet being raised out of solution to mount the network.

for 5 minutes to further improve adhesion to the new substrate and drive off any remaining solvent, the temperature was kept below 80°C to prevent damage to the PET.

3.2.3 Metal Assisted Chemical Etching (MACE)

Porous silicon is a nanocrystalline form of silicon which has attracted a great deal of research interest for its unusual optoelectronic behaviour.⁵⁹ A number of devices based on crystalline silicon nanowire with sections of porous silicon have demonstrated enhanced performance as photodetectors compared to corresponding devices without porosity.⁶⁰⁻⁶¹ A process was developed to introduce porous silicon regions into the seamless Si NWN and the effects of this structural modification on the photovoltaic behaviour of the device were investigated.

A multitude of pSi fabrication techniques have been developed with by far the most commonly used process being electrochemical anodisation in HF based electrolytes. Such processes result in a regularly structured porous film of uniform thickness atop an underlying compact Si layer.⁶² To avoid issues with electrically contacting through a highly resistive pSi top layer, a metal assisted chemical etch (MACE) based porosification technique was developed to introduce discrete zones of porosity in the nanowire structure. In MACE, pSi formation is catalysed using noble metals (Au, Ag, Pt) allowing for control over the regions where porosification takes place.

The first step of the network porosification process was the e-beam deposition of a 5 nm Au film onto a clean SiO₂ substrate. This gold film was then heated at 500°C for 10 minutes to produce a dewetted pattern of nanoparticles with an average diameter of 40±15 nm shown in figure 3.9. (a) and (b). Secondly, the underlying SiO₂ film was etched in a 15ml solution of aqueous HF (48% v/v), H₂O₂ (30% v/v) and DI H₂O in a 2:1:5 volume ratio to disperse the Au NPs in a metastable suspension. Finally, the fabricated Si NWN described previously is placed in the prepared solution for 1 minute to yield a random pattern of pores uniformly distributed across the nanowire network structure. The porosified network is then removed and rinsed in DI H₂O for 5 minutes to quench the etching process.

When the silicon network is placed in the etching solution, Brownian motion⁶³ drives the suspended gold NPs to randomly collide against the silicon surface. At the point

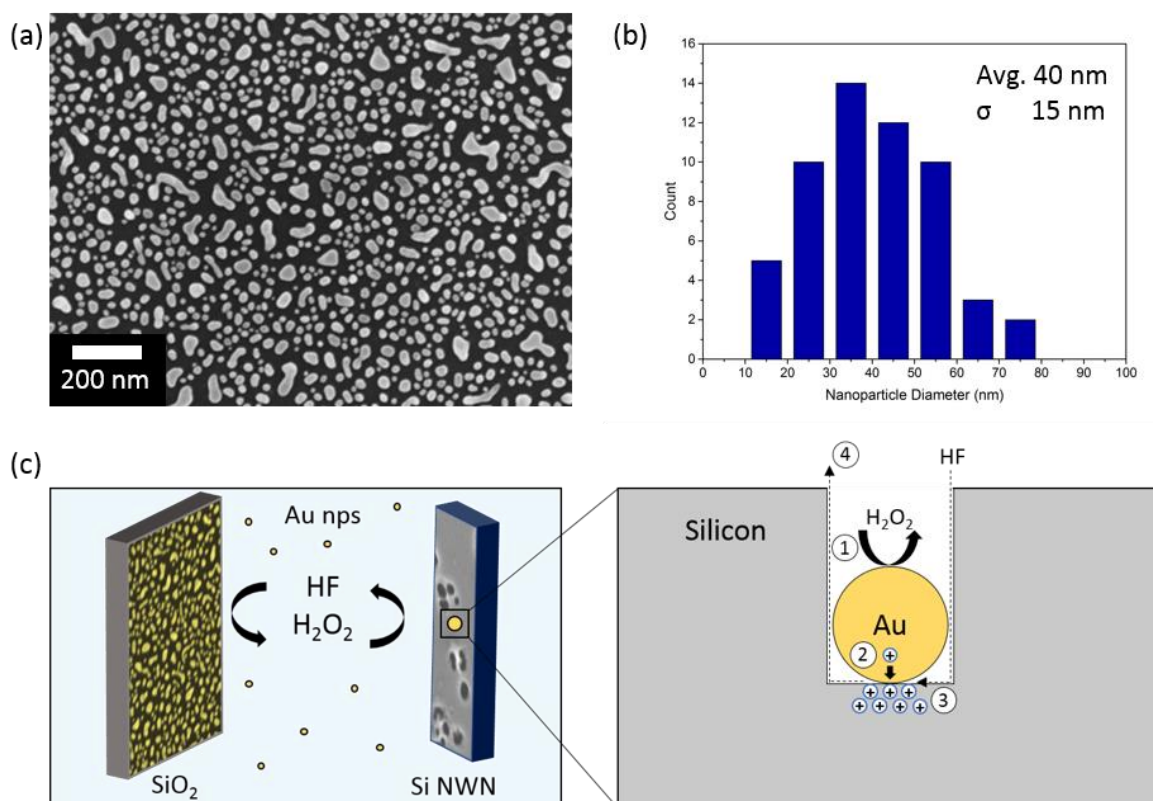
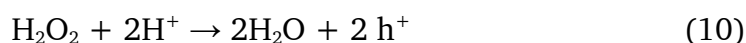


Figure 3.9. (a) SEM image of 5 nm Au film dewetted at 500°C, (b) Diameter distribution of dewetted gold nanoparticles (measured from 55 particles), and (c) A schematic of the [HF-H₂O₂] solution based MACE process used to introduce localised p-Si sections in the Si nanowire network: (1) Catalytic H₂O₂ reduction (2) Hole injection (3) HF dissolution of oxidised silicon (4) Diffusion of reaction products away from active reaction site at the pore tip.

of contact, the gold catalyses the local oxidation of silicon which is then etched by HF. The chemistry underlying the MACE process is reasonably well understood, although the exact nature of the reaction intermediates involved is still debated.⁶⁴⁻⁶⁶ It is generally accepted that the surface of the gold particle catalyses the reduction of H₂O₂ as shown below in equation (10).⁶⁷ The observation of hydrogen evolution during etching has been suggested to be due to the secondary reduction reaction shown in equation (11).⁶⁸

Metal Cathode Reactions:



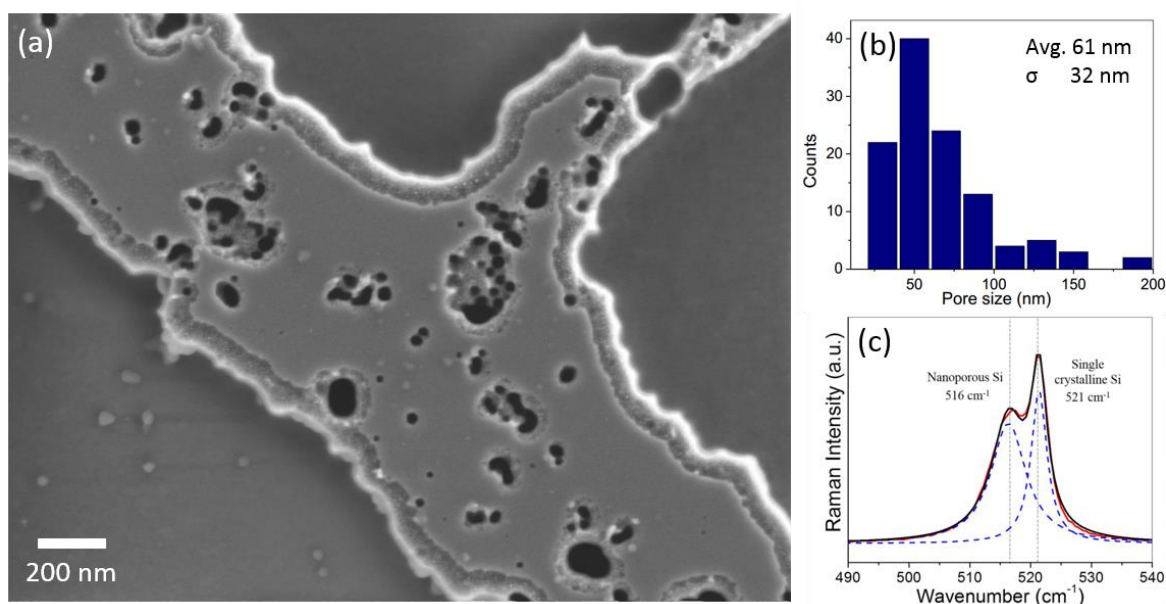
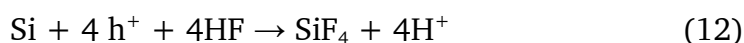
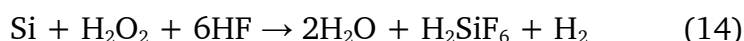


Figure 3.10. (a) High resolution SEM image of silicon nanowire showing pores randomly distributed across surface, (b) Distribution of pore sizes as measured from SEM imaging (calculated from 120 pores), and (c) Raman spectra of porosified silicon nanowire network (blue dotted lines indicate deconvoluted peaks) showing both single crystalline, and porous silicon signals.

Silicon Anode Reactions:



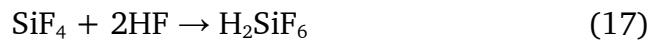
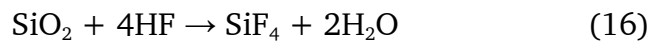
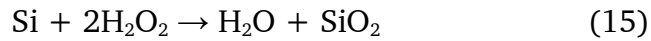
Overall Reaction:



As a result of this reduction, holes are formed and are injected into the silicon surface beneath as shown in figure 3.9 (c). The underlying Si substrate is then oxidised by the injected holes and subsequently dissolved by HF which readily diffuses between the Si-Au interface.⁶⁹ Fluorosilicic acid is produced as a by-product of the etch reaction and diffuses away from the active site. As the reaction is catalysed at the point of contact between the Au NP and the silicon, the pore depth increases with etch time. The most widely accepted mechanism for the final HF silicon etching step involves the direct dissolution of the silicon and the subsequent formation of hexafluorosilicic acid (equations (12) and (13)). The overall reaction is summarised in equation (14); as mentioned previously, other silicon oxide intermediate species

have been proposed to be involved in the reaction.⁶⁶ These may contribute to the overall reaction scheme but direct evidence for these species has not yet been reported due to the difficulties associated with *in situ* monitoring of the etch process.

Figure 3.10 is a SEM image of a section of the porosified NWN that shows a random spatial distribution of pores across the surface of the wires. The pore density within the area of the nanowire network was determined to be $24 \mu\text{m}^{-2}$ and the average pore diameter was measured as 61 ± 32 nm, slightly larger than the average size of the original gold nps 40 ± 15 nm. This discrepancy is attributed to two factors; firstly, larger particles may be formed by fusion during collisions of the unpacified gold nps in suspension. The elliptical profile of the larger pores also suggests these were formed by two fused spherical particles. Secondly, in parallel with the catalysed etching reaction, a general silicon dissolution process will occur in a HF/H₂O₂ solution as detailed in equations (15), (16) and (17). This isotropic etching process will naturally occur most rapidly at high surface area points such as the pore rim, widening the width of the pore as the etch time is increased.



It is well-documented that the MACE process results in a thin coating of pSi along the interior surface of the etched pores.⁷⁰⁻⁷² The presence of porous silicon within the nanowire structure was verified using Raman spectroscopy. As shown in figure 3.10 (c), a signal corresponding to single crystalline silicon⁷³ was observed at 521 cm^{-1} and a clear shoulder peak at 516 cm^{-1} matches with reported values for MACE fabricated porous silicon.⁷⁴⁻⁷⁵

Further structural examination was performed using TEM analysis of a porosified silicon nanowire as shown in figure 3.11 (a). Dark regions on the wire body can be

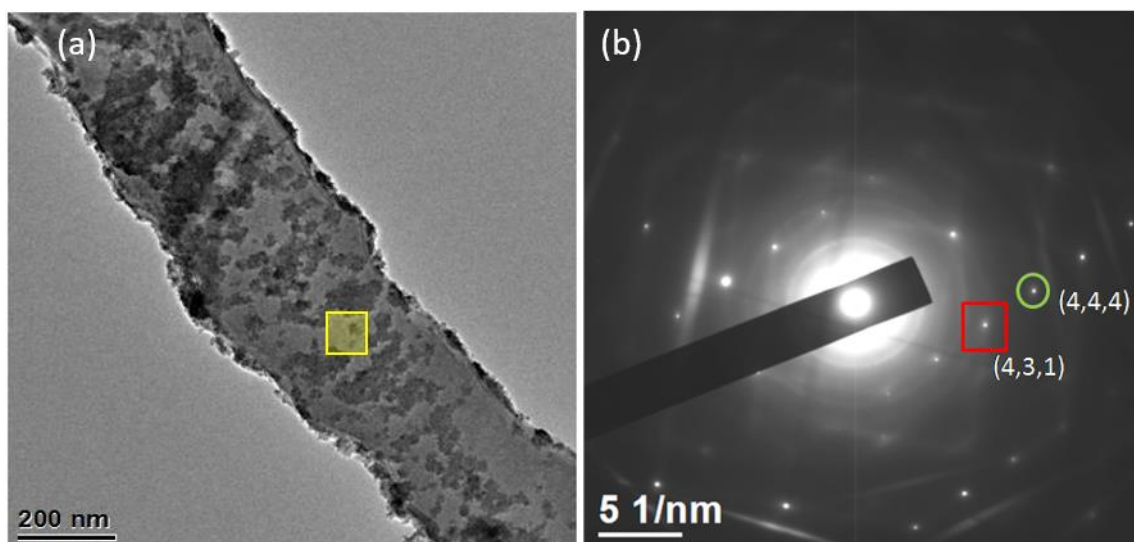


Figure 3.11. (a) TEM image of porosified single crystal silicon nanowire and (b) corresponding SAED pattern taken from yellow highlighted region.

observed corresponding to the porous silicon sites; the contrast is attributed to increased scattering of the electron beam in the rough nanocrystalline pores compared to the single crystal wire body. A selective area electron diffraction (SAED) pattern, shown in figure 3.11 (b), was obtained from a central region of the Si nanowire which clearly demonstrates that the original single crystal structure is preserved after the porosification process.

3.2.4 Electrical and Optical Behaviour

The previously described procedure was developed to fabricate an interconnected silicon nanowire network with seamless junctions and mounted on a transparent, flexible PET substrate. In this section, the optoelectronic behaviour of this device was studied with particular attention focussed on its application as a transparent and flexible photodetector. In order to make electrical measurements on the network, the surface oxide layer was first etched in 2% aqueous HF solution for 30 seconds. Following a thorough rinse in DI H₂O for 2 minutes, a shadow mask was placed over the network area and a 50 nm gold film with a 5 nm titanium adhesion layer was deposited using an ebeam vacuum deposition system. The sample was masked and placed under vacuum within 10 minutes of the HF etch to minimise ambient oxidation. An additional 250 nm of nickel was then deposited to ensure good

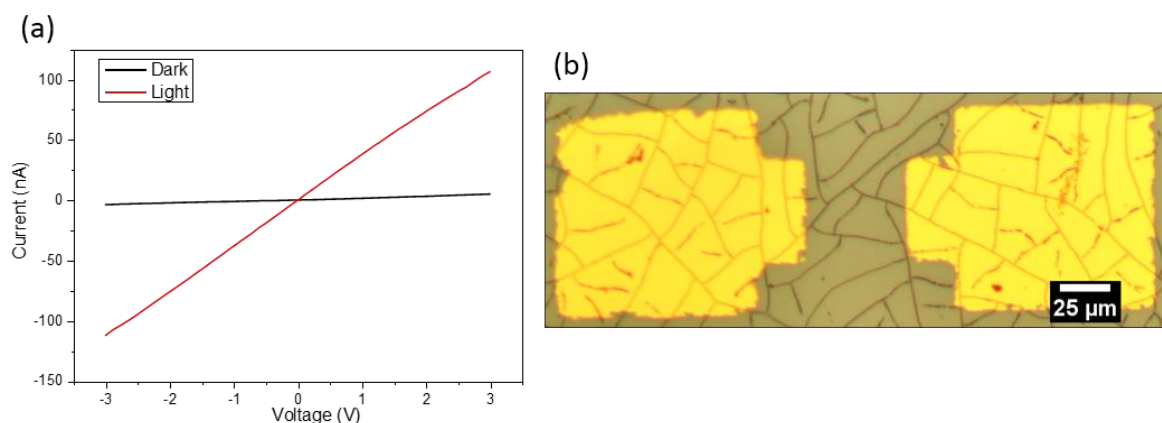


Figure 3.12. (a) Current-voltage graph of 50 μ m device measured in dark and under 100mW/cm² white light illumination (b) Optical image of a contacted Si NWN device with 50 μ m electrode separation.

connection to the 260 nm thick nanowires, finally a 10 nm gold layer was deposited to cap the nickel and prevent oxidation. Figure 3.12 (b) shows an optical image of the 50 μ m contact pads used for electrical characterisation.

An IV graph of the contacted Si NWN device is shown in figure 3.12 (a), voltage was swept between -3V and +3V and plotted against the current measured. This measurement was performed in dark and then again under white light illumination. A linear ohmic response was observed across both polarities of the sweep demonstrating that no Schottky barriers were formed at either contact.⁷⁶ An ohmic connection avoids any Schottky contact based optical interactions⁷⁷ from affecting the device response and so any observed behaviour could be attributed entirely to the optoelectronic characteristics of the Si NWN itself. A pronounced photoresponse was also observed; the device resistance under white light illumination differed from its dark resistance state by a factor of ~ 30 . Further measurements were performed varying the white light intensity while the voltage was held constant at 2V. Figure 3.13 (a) shows the linear response of the devices photocurrent with no saturation observed across the range of illumination intensities tested.

The transmission spectrum of a PET mounted Si NWN over the entire visible spectrum is shown in figure 3.13 (b). A relatively uniform transmission level was

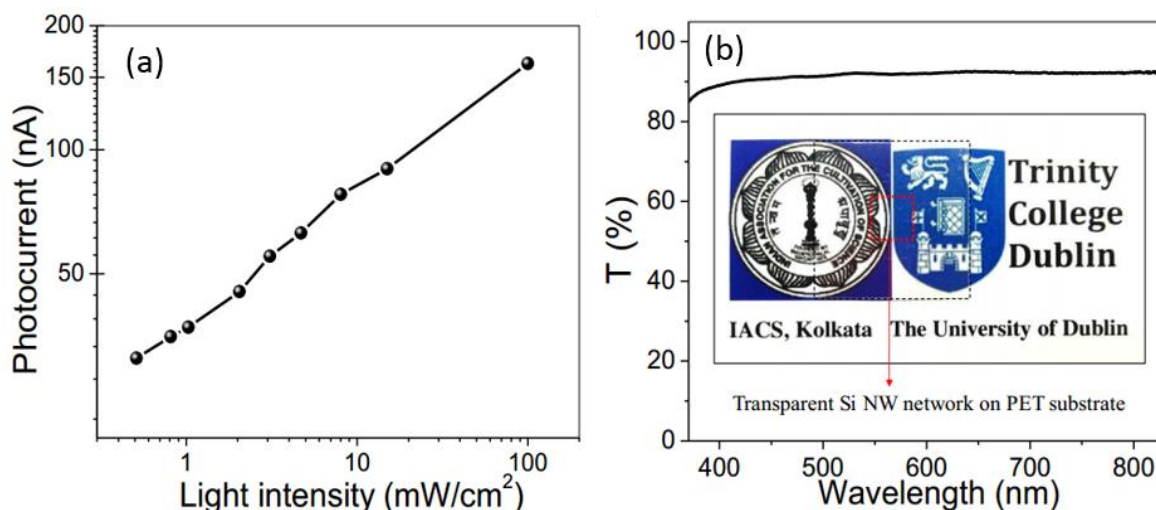


Figure 3.13. (a) Photoresponse of device under white light illumination across a range of intensities showing a linear trend (b) Substrate normalised transmission spectrum of PET mounted Si NWN device measured between 350 nm and 850 nm.

observed across all measured wavelengths, notably the observed transparency of 92% at 550 nm is higher than would be expected given the 12% fill factor measured from analysis of SEM images. The increased network transmission is attributed to damage during the transfer process decreasing the final network area and also the diffraction of light around the edges of the nanowires.⁷⁸ The decreasing transmission below 400 nm is caused by the high absorption of the PET substrate in the near UV region.⁷⁹ The high optical transparency of the Si NWN naturally implies a low absorptivity, however the large photocurrent measured indicates that the active network area must be highly efficient at carrier generation. The proposed photoconduction mechanism of the Si NWN is discussed in detail in section 4.2.4.3.

3.2.4.1 Time Dependency

The response time of a device is an important parameter to describe its performance as a photodetector, this property measures the devices ability to respond electrically to high-speed optical signals. Figure 3.14 (a) shows a schematic of the experimental setup used to test the time dependency of the Si NWN photoresponse. A 3 mW 650 nm laser was used as a light source in combination with a variable frequency optical chopper (THOR labs MC 2000B-EC) and the photoresponse of the device was measured through application of a 2V bias. Figure 3.14 (b) shows the device current

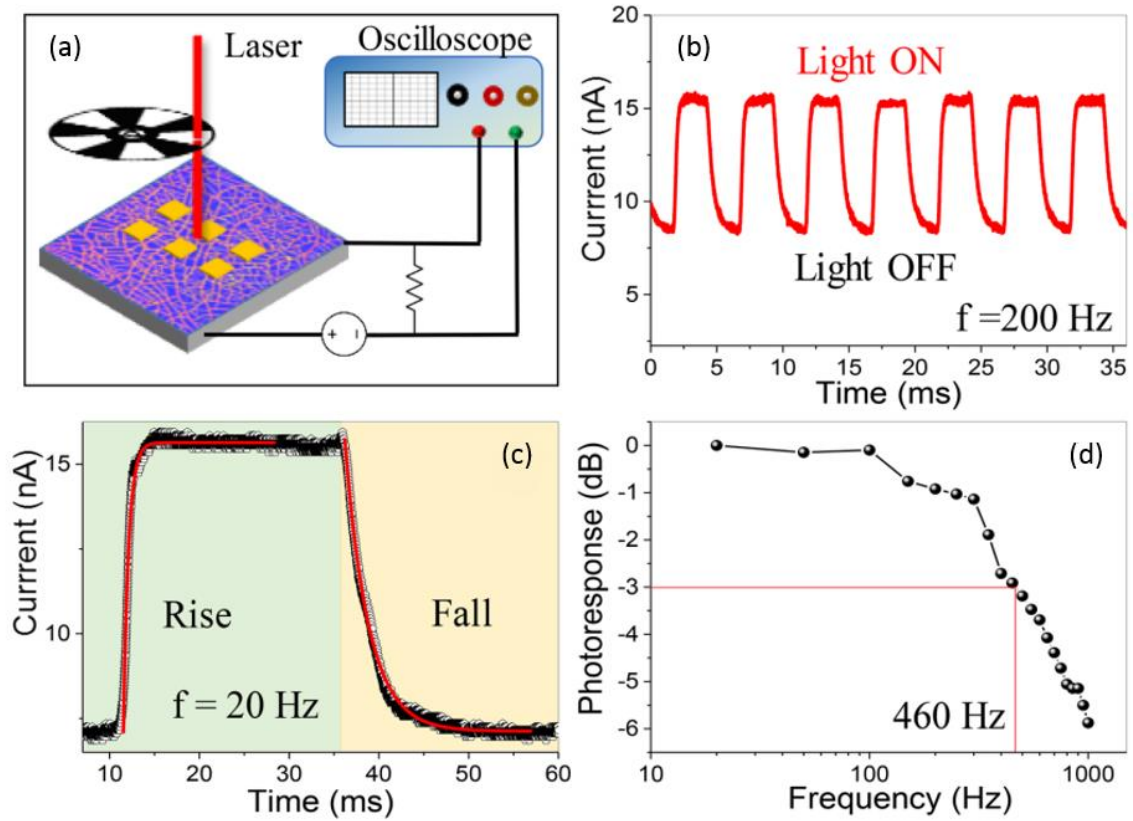


Figure 3.14. (a) Schematic of experimental setup used for response time measurements using an optical chopper (b) Current-Time graph of device behaviour under light/dark cycling at a frequency of 200Hz (c) Individual on/off cycle measured at low frequency for rise and fall time constant calculations (d) Normalised photoresponse plotted against signal frequency with cut off frequency f_{3dB} 460Hz highlighted.

response to 7 light/dark (ON/OFF) cycles with 200 Hz frequency, saturation of both the ON and OFF resistance states is reached. Over the course of this signal modulation experiment, the photoresponse was demonstrated to be stable and reproducible over multiple cycles.

The rise and fall response times of the device were calculated using the exponential equations shown in (18) and (19) respectively,⁸⁰ where I = current, I_0 = Initial current, A_1 = Independent fitting variable, x = time, t_r = rise time and t_f = fall time. An individual light/dark cycle taken at 20 Hz is shown in figure 3.14 (c); at this low frequency, clear saturation dark and light current levels were visible and were used in the calculation. The rise and fall times were estimated at 0.58 ms and 1.82 ms respectively.

$$I = I_0 - I_0 \times e^{(-x/t_r)} \quad (18)$$

$$I = I_0 + A_1 \times e^{(-x/t_f)} \quad (19)$$

Another important parameter of a photodetector is the cut off frequency (f_{-3dB}) which is defined as the modulation frequency at which the device response becomes half of its initial value.⁸¹ Figure 3.14 (d) represents the normalised photoresponse plotted against the applied signal frequency from 20 Hz to 1000 Hz. At low frequencies below 100 Hz, the photoresponse is relatively constant and this is taken as the reference saturation value. The frequency at which this value halved was estimated to be 460 Hz.

3.2.4.2 Wavelength Dependency

The wavelength dependency of the Si NWN photoresponse was studied using monochromatic light sources. Figure 3.15 (b) shows the IV behaviour of the device under illumination of 800 nm, 700 nm, 600 nm and 500 nm filtered white light sources and in dark and a general trend of increased response with decreasing wavelength was observed. The responsivity of the device (R_λ) was also investigated with respect to the wavelength of the applied light source. Spectral responsivity is measured in units of $A.W^{-1}$ and is defined in equation (20) where: I_p = photocurrent (A), A = device area (cm^2) and P_λ = input light intensity ($W.cm^{-2}$). The active area of the network was analysed using SEM and determined to be 12 % of the total device area. Figure 3.15 (c) illustrates the relationship between applied wavelength and device responsivity showing a clear trend of increasing photoresponse toward higher energy wavelengths. The responsivity was seen to increase from 4.9 to 24.6 $A.W^{-1}$ as wavelength decreased from 950 nm to 350 nm. The peaks at 520 nm and 650 nm have corresponding band gaps of 2.39 eV and 1.91 eV respectively and correlate to the widened band gaps of the nanocrystalline silicon sections within the network.⁸² Increases in material band gap above bulk values⁸³ correspond to decreases in particle size and as such the presence of these shallow but distinct peaks could

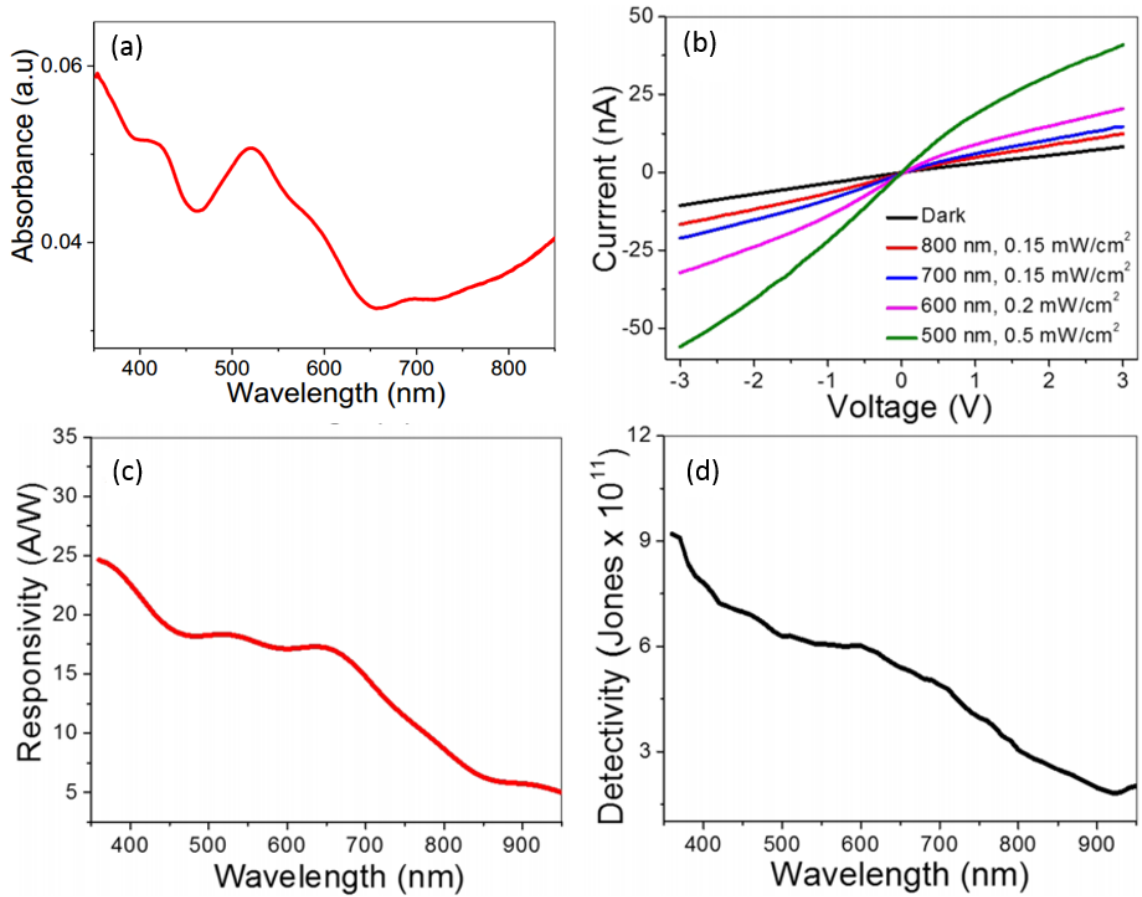


Figure 3.15. (a) UV-Vis absorption spectrum of PET mounted Si NWN (b) IV of device under different individual wavelengths and (c) Responsivity and (d) Detectivity as a function of light wavelength under a bias of 2V.

suggest certain sizes of porous silicon are preferentially formed during the MACE process.

This trend is in agreement with the UV-Vis absorption spectrum shown in figure 3.15 (a) which also displays a general increase in absorption at lower wavelengths

$$R_{\lambda} = \frac{I_p}{A \times P_{\lambda}} \quad (20)$$

Another important figure of merit for characterising the performance of a photodetector is detectivity (D_{λ}) which is measured in Jones ($\text{cm} \cdot \text{Hz}^{0.5} \cdot \text{W}^{-1}$); it is defined in equation (21) where R_{λ} = spectral responsivity ($\text{A} \cdot \text{W}^{-1}$), q = charge of electron (C) and J_d is the dark current density ($\text{A} \cdot \text{cm}^{-2}$). The detectivity value of

9×10^{11} Jones measured at 350nm is comparable to photodetectors based on bulk Silicon (4×10^{12} Jones).⁸⁴

$$D_{\lambda} = \frac{R_{\lambda}}{\sqrt{2q \times J_d}} \quad (21)$$

The spectral dependency trend observed in the cases of device absorption and responsivity, i.e. both increasing at lower wavelengths is also demonstrated with the detectivity of the device. This behaviour is attributed to quantum confinement effects within the pSi sections of the network and this property of the device is further examined in section 3.2.4.3.

3.2.4.3 Photoconduction Mechanism

In order to study the effect of the presence of pores on the devices photovoltaic behaviour an unporosified Si NWN was fabricated. The IV behaviours of a porous and non-porous device under light and dark conditions are shown in figure 3.16 (a) and (b) respectively. The photosensitivity,⁸⁵ defined as $((I_{\text{light}} - I_{\text{dark}})/I_{\text{dark}}) \times 100\%$, under white light illumination of 100 mW.cm^{-2} intensity was calculated to be $\sim 2000\%$ for the network with pores and only 300% for the non-porous network calculated at a bias of 2V.

$$\text{EQE} = \frac{h \times c \times R_{\lambda}}{e \times \lambda} \times 100\% \quad (22)$$

The external quantum efficiency⁸⁶ (EQE) of the porous and non-porous Si NWNs were measured based on the definition of EQE given in equation 21; h = Plancks constant, c = speed of light in vacuum, R_{λ} = spectral responsivity, e = charge on an electron and λ = wavelength. Opposing trends are observed in wavelength dependency of the EQE in the two network types. In the case of the non-porous crystalline Si NWN, the EQE is seen to decrease as the light wavelength drops below 500 nm which is attributed to the high reflection coefficient and shallow penetration depth of UV light.⁸⁷⁻⁸⁸ However, in the case of the porosified network the EQE is seen to rise steadily as wavelength is decreased which is in agreement with the measured

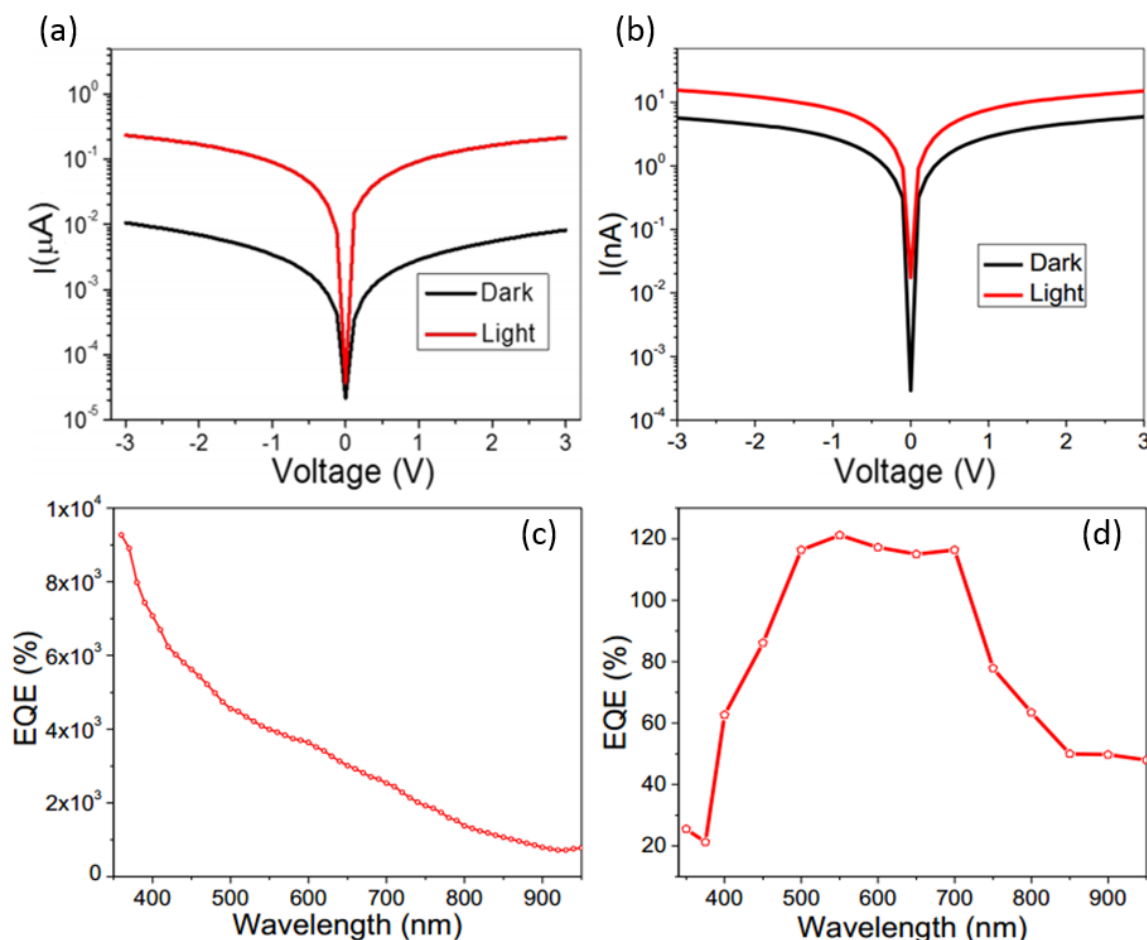


Figure 3.16. (a) Dark and white light (Intensity: $100\text{mW}/\text{cm}^2$) IV of silicon NWN (a) with pores and (b) without pores, External quantum efficiency as a function of wavelength for a (c) porous and (d) non-porous Si NWN.

absorption spectrum (figure 3.15 (a)). This trend is attributed to the roughness of the pores leading to a reduction of incident light reflection. Additionally, localised energy states generated from surface defects in the porous network segments can act as recombination traps for injected charge carriers.⁸⁹ In dark conditions these traps result in low current levels but when placed under illumination, charge carriers can be excited from these states into the conduction band and increase the photocurrent of the device. Higher energy photons can excite a broader range of localised states than lower energy photons leading to an increase in EQE with decreasing wavelength.⁹⁰ This control experiment highlights the importance of the pSi sections for high performance of the Si NWN as a photodetector. The high transparency of the device necessitates a low fill factor and so in order to obtain a large responsivity, the small active area of the device must display high efficiency for carrier generation.

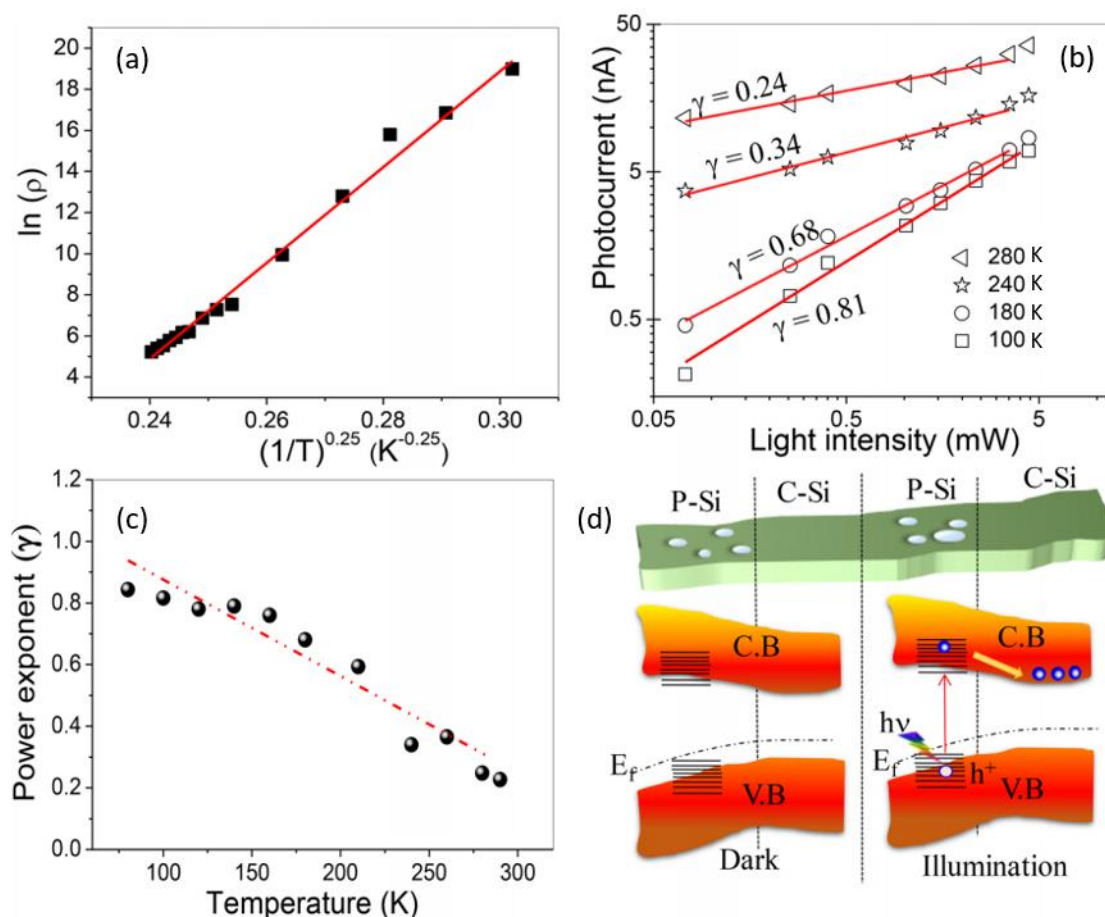


Figure 3.17. (a) Temperature dependence of device resistivity in dark and (b) Photoresponse, (c) Relationship of power exponent to temperature⁹¹ (d) Schematic representation of porous Si NW under dark and light conditions featuring photon induced carrier excitation to conduction band.

The observed behaviour is in agreement with previous reports on the performance of porous and non-porous silicon nanowire photodetectors.⁶¹ Further investigation of the electron transport mechanism was conducted with low temperatures measurements performed both in dark conditions and under white light illumination of varying intensities. Figure 3.17 (a) shows the temperature dependence of device resistivity in dark measured between 100 K and 325 K. A linear relationship was observed between $\ln(\rho)$ and $T^{-0.25}$ and this behaviour is consistent with 3D Mott variable range hopping (VRH) mechanism⁹¹ which is defined in equation (23) where; ρ_0 = characteristic resistivity (ohm.m), T_0 = characteristic temperature (K), T = temperature (K) and d = dimensionality. Due to the large 260nm height of the nanowires the dimensionality is 3 for this system resulting in an exponent value of -0.25 which was verified by the linear fit in figure 3.17 (a). The density of states near

the Fermi energy⁹¹ can be estimated using equation (24) where; T_o = characteristic temperature (K), k_b = Boltzmann constant and ζ = localisation length (m). Assuming the localisation length⁹² to be 0.3 nm and taking a value of $T_o = 2.8 \times 10^9$ K from figure 3.17 (a), the density of states is calculated to be $\sim 10^{19} \text{ eV}^{-1} \cdot \text{cm}^{-3}$ which is comparable to values measured for polycrystalline silicon.⁸⁹

$$\rho(T) = \rho_o \exp\left[(T_o / T)^{1/(d+1)}\right] \quad (23)$$

$$N(E_f) = \frac{21.1}{k_b \times T_o \times \zeta^3} \quad (24)$$

The VRH mechanism suggests that the observed photoconduction in the Si NWN is due to the hopping of charge carriers between localised trap states.^{91, 93} The photocurrent was seen to monotonically increase with higher intensities of light, additionally the rate of increase was seen to have a temperature dependence as demonstrated in figure 3.17 (b). The relationship between photocurrent and light intensity followed a power law of the form ($I_p \propto P^\gamma$) where γ increased from 0.24 to 0.81 as the temperature was decreased from 325 K to 100 K shown in figure 3.17 (c). This gradual change from sublinear to a linear response is consistent with electronic doping by localised trap states⁹⁴ and has previously been observed in Si and GaN nanowires.⁹⁵⁻⁹⁶

Figure 3.17 (d) depicts a schematic energy band diagram of a porous Si NW in both dark and light conditions. Localised energy states resulting from pSi surface defects acting as traps for injected charge carriers leading to a high device resistance in the dark. Quantum confinement results in pSi having a larger bandgap than cSi, and so UV light can be efficiently absorbed and excite a broad range of localised trap states.⁹⁰ Hence the porous regions of the nanowires act as reservoirs of charge carriers which can be excited to the conduction band in the presence of light. The relative band alignment allows the excited carriers to be swept into the adjacent crystalline silicon regions and can easily reach the electrodes due to the seamless nature of the junctions resulting in the high photoresponse observed.

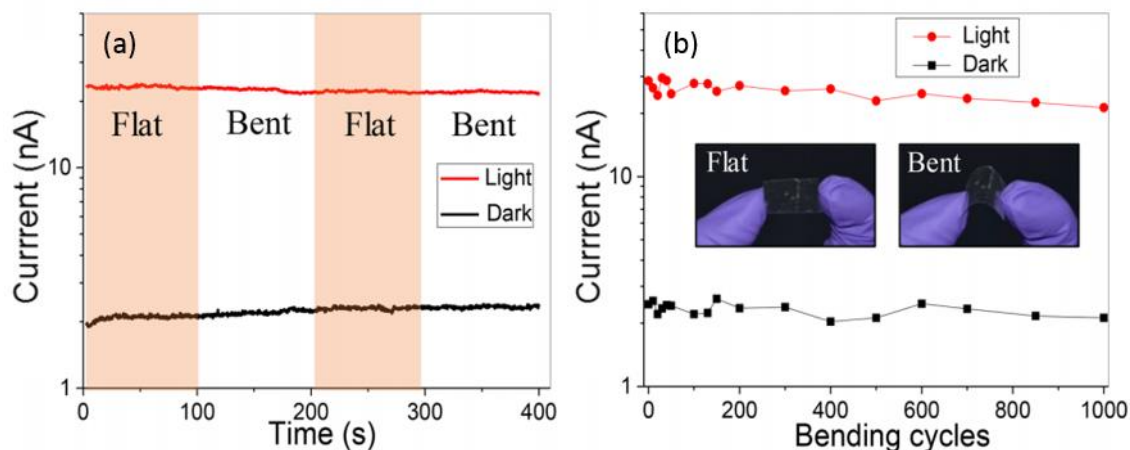


Figure 3.18. (a) Time dependant IV plot of the porous Si NWN mounted on a PET substrate showing stability of device performance during flexibility tests and b) dark and light current values over 1000 bending cycles to a 5 mm bending radius.

3.2.4.4 Flexibility Studies

The performance of the PET mounted Si NWN was tested over a number of light/dark cycles and was shown to be stable during high frequency signal modulation (figure 3.14 (b)). In this section, the device performance was measured during flexing of the network to a 5 mm bending radius and compared to its performance under normal flat conditions. Figure 3.18 (a) illustrates the device current in both dark and light over multiple bending cycles and, importantly, no change in behaviour was observed between flat or bent device states. The stability of the device photoresponse was demonstrated over 1000 bending cycles as shown in figure 3.18 (b) and is unchanged throughout the measurement. The device stability is attributed to the seamless junction geometry which is not prone to the sliding movements observed in networks of individual nanowires.⁹⁷

3.3 Conclusions

In this chapter, the development of a novel fabrication process for silicon nanowire networks with seamless junctions has been described in full and the device performance as a transparent and flexible photoconductor has been demonstrated. A scalable crack templating technique utilising an acrylic nanoparticle suspension was studied and a reproducible spin coating procedure for the formation of an

interconnected void template with an average crack width of 902 ± 236 nm was designed. An interconnected Ti/Au network was fabricated on an SOI substrate *via* metal deposition using the crack template as a mask. This metal structure was then used as a mask during a plasma etching process to transfer the seamless pattern onto the underlying silicon device layer. The metal network was removed through a series of selective chemical etches to remove both the gold and titanium layers and SEM characterisation of the resulting silicon network gave an average nanowire width of 870 ± 240 nm. A passive voltage contrast technique and image thresholding analysis were used to quantify the percentage of nanowire segments that were disconnected from the main network body which was calculated at $33.4 \pm 6.2\%$. A float transfer procedure using a photoresist mesh support was developed to mount the silicon network on a transparent and flexible PET substrate. Au nanoparticles with an average diameter of 40 ± 15 nm were formed *via* dewetting of a 5 nm gold film at 500°C and were dispersed in a $\text{HF}/\text{H}_2\text{O}_2$ solution. A metal assisted chemical etch process was carried out to introduce localised regions of porous silicon within the crystalline network structure. An average pore diameter of 61 ± 32 nm and area density of $24 \mu\text{m}^{-2}$ were measured in SEM; Raman spectroscopy and TEM were used to verify both the presence of nanocrystalline silicon within the porous sections and the crystallinity of the surrounding network structure.

Electrical interrogation of the Si NWNs was achieved *via* metal evaporation of a Ti/Au/Ni/Au layer through a shadow mask to form contact pads and the performance of the network as a transparent and flexible photodetector was investigated. Ohmic IV behaviour was observed during voltage sweeps and a linear photoresponse was demonstrated over a range of light intensities at a constant applied bias. The transmission of the PET mounted Si NWN was measured to be 92% at 550 nm and remained constant across the visible wavelength range tested. A rise time of 0.58 ms and a fall time of 1.82 ms were estimated using exponential fits to a light/dark cycle at a frequency of 20Hz at a bias of 2V. A cut off frequency ($f_{\text{-3dB}}$) of 460Hz was calculated, and responsivity and detectivity were both observed to increase at higher energy wavelengths with respective values of 24.6 A.W^{-1} and

Ref.	Active Material	T (%)	Spectral Range (nm)	Detectivity (Jones)	Responsivity (A/W)	Rise Time (s)	Flexible, cycles
95	ZnO-CdO	95	400-800	--	1	3	Yes, 200
96	InGaZnO	80	350	--	--	--	No
97	SnO ₂ nanobelt	86	UV	--	--	--	Yes
98	InZnO-CdS	85	400-800	--	0.054	--	No
99	ZnO-SnO ₂	90	250-630	--	--	8-32	--
100	Zn ₂ SnO ₄	80	UV	--	--	0.8-3	Yes
101	ZnO	90	UV	10 ¹⁰	0.01	3.3-20	Yes
102	Graphene	90	---	--	2.6x10 ⁻⁵	21-25	Yes
103	WSe ₂	72	370-1064	--	0.2-1	0.9-2	Yes
104	WS ₂	60	--	--	--	51	No
105	In ₂ Se ₃	63	254-1064	6.02x10 ¹²	20.5	2.46x10 ⁻²	Yes
106	WO ₃ -Ag	82	400-700	--	0.01	1	Yes
107	NiO	70	400	9.6x10 ¹³	3.8	2.4x10 ⁻²	No
108	Cu ₄ O ₃	72	450-625	--	--	3.8x10 ⁻²	No
109	Cyanine Dye	68	455-625	10 ¹²	0.165	--	--
110	V ₂ O ₅	77	455-620	1.45x10 ¹⁰	0.02	4.9	Yes
111	MoS ₂ -Graphene	70	455-620	1.8x10 ¹⁰	1.23x10 ⁻²	10	No
This work	Si NWN	92	350-950	9x10¹¹	25	0.58x10⁻³	Yes, 1000

Table 3.2. Si NWN performance compared to transparent photodetectors from literature.⁹⁸⁻¹¹⁴

9x10¹¹ Jones at 350 nm. A comparison against an unporosified crystalline Si NWN demonstrated the importance of porous silicon to the device performance. For a porous network, the EQE was seen to steadily increase with decreasing wavelengths, while the EQE of an unporosified device dropped off below 500 nm. This behaviour was attributed to increased light absorption around the rough pore sites and the high UV reflection coefficient of crystalline silicon. Low temperature IV studies under light and dark conditions provided evidence for a 3D Mott variable range hopping mechanism and charge carrier hopping between localised trap states at the pore sites was proposed as a mechanism of the observed photoconduction behaviour.

The device performance was demonstrated to be stable during flexibility tests to a bending radius of 5 mm, and the on/off ratio was unchanged over 1000 bending cycles. Table 3.2 compares various figures of merit of the porous Si NWNs fabricated during this work alongside other transparent photodetector devices collected from literature which illustrates their high performance in this field. Additionally, the tendency for silicon to form a passivating oxide layer¹¹⁵ aids the stabilisation of the device, showing no change in photovoltaic behaviour after two months of storage in ambient atmospheric conditions.

3.4 References

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Nanofibre Templated Aluminium Nanowire Networks

Silver nanowire networks have emerged as promising candidates to replace indium tin oxide thin films as the dominant material for transparent conductors. However, large junction resistances present between nanowires necessitate the use of aggressive post processing treatments to achieve high device performance. Additionally, the susceptibility of nanostructured silver to degradation from atmospheric sulfur compounds has raised serious concerns about the long term stability of devices based on these materials. This chapter details the development of a templating strategy for the top down fabrication of interconnected aluminium nanowire networks patterned from networks of electrospun PMMA nanofibres. The optimisation of a polymer based pattern transfer process is studied and the performance of the templated networks as transparent conductors is investigated.

4.1 Introduction

Materials which possess both optical transparency and electrical conductivity are known as transparent conductors (TCs) and are essential components in many everyday optoelectronic devices such as touchscreens,¹⁻² LEDs³⁻⁴ and solar cells⁵⁻⁶. The high visible light transmission and tuneable sheet resistance values offered by indium tin oxide (ITO) thin films have deservedly made it the material of choice for the vast majority of TC applications.⁷⁻⁹ However issues such as the scarcity of indium,¹⁰⁻¹¹ a costly and slow sputtering process¹²⁻¹³, poor transparency to UV and IR wavelengths¹⁴ and brittle mechanical behaviour¹⁵ disincentivise the continued use of ITO for next generation optoelectronic devices. These and other disadvantages have motivated the search for alternative TC materials and thus far percolative networks of silver

nanowires (NWN) have demonstrated the best performance in terms of transmission and conductivity.¹⁶⁻¹⁸

However, a number of issues exist concerning the feasibility of utilising silver NWNs for device manufacture on an industrial scale. Silver nanowires are generally synthesised using a solution based polyol process which relies upon the formation of a thin coating of polyvinylpyrrolidone (PVP) around the surface of the nanowires to direct anisotropic growth.¹⁹⁻²⁰ When formed into a network, this insulating polymer shell results in large contact resistances at the nanowire junctions limiting the overall device performance.²¹ Post fabrication processing steps such as thermal annealing²²⁻²³ or mechanical pressing²⁴⁻²⁵ are necessary to maximise network conductivity which restricts the choice of substrates. Additionally, the reaction of silver with atmospheric sulfur compounds is well documented²⁶⁻²⁹ and the high surface area to volume ratio of silver nanowires leaves them especially vulnerable to corrosion. Sulfur containing species such as H_2S , SO_2 and OCS can originate from either the combustion of fossil fuels or from natural sources and these compounds have been detected at significant concentrations throughout the world.³⁰⁻³¹ TEM analysis of PVP coated silver nanowires stored under ambient conditions have shown that considerable sulfidation of these materials can readily occur on a timescale of only a few weeks.³² Without additional protective measures, the poor device lifetime of silver NWNs remains a significant problem and inhibits their widespread application.³³

Despite these shortcomings, the device form factor demonstrated by NWNs (i.e. a conductive metallic mesh with voids allowing for optical transmission) remains a viable material engineering strategy for TC design. As discussed in chapter 1, a large number of publications have reported on the fabrication of NWNs with seamless junctions and detailed their ultra-high performance as TCs.³⁴⁻³⁸ However, the commercial scale production of these structures is limited by either reliance upon slow direct-write lithography steps or the requirement for freestanding transfer processes. Furthermore, these devices are typically fabricated with silver or copper, both of which are prone to environmental sulfidation.²⁸ In terms of electrical conductivity, aluminium ranks fourth overall displaying a bulk resistivity only ~ 1.7

times higher than silver, and as one of earths most abundant elements, it is available at a raw cost of less than 0.4% that of silver.³⁹⁻⁴⁰ Aluminium also passivates in air to form a thin, highly stable surface oxide which protects the underlying metal from corrosion. Despite these promising material properties, a very small number of reports have been made on networks of aluminium nanowires as TCs and all have demonstrated insufficient performance to be seriously considered for most applications.^{34, 41}

In this chapter, the development of a scalable fabrication method for seamless aluminium NWNs with superior performance to both silver NWNs and ITO films is detailed. The fabrication technique relies upon a novel pattern transfer process to form a metal deposition template mapped off the structure of a randomly oriented network of PMMA nanofibres. The optimisation of the electrospinning process used in their formation is discussed and each stage of the pattern transfer process is described in full. The templated aluminium NWNs are characterised in terms of standard TC figures of merit and a materials by design strategy for the fabrication of low cost TCs with tuneable optical and electrical behaviours is proposed.

4.2 Results

In this section, the development of a patterning technique for the fabrication of a deposition template mapped from a PMMA nanofibre network is detailed in full. The electrospinning process parameters are investigated and optimised for the formation of smooth uniform PMMA nanofibres with tuneable diameters. The various stages of the pattern transfer process are discussed in turn and the fidelity of the templated structures versus the original nanofibres is examined. The performance of the fabricated aluminium nanowire networks as transparent conductors is also explored and discussed in detail.

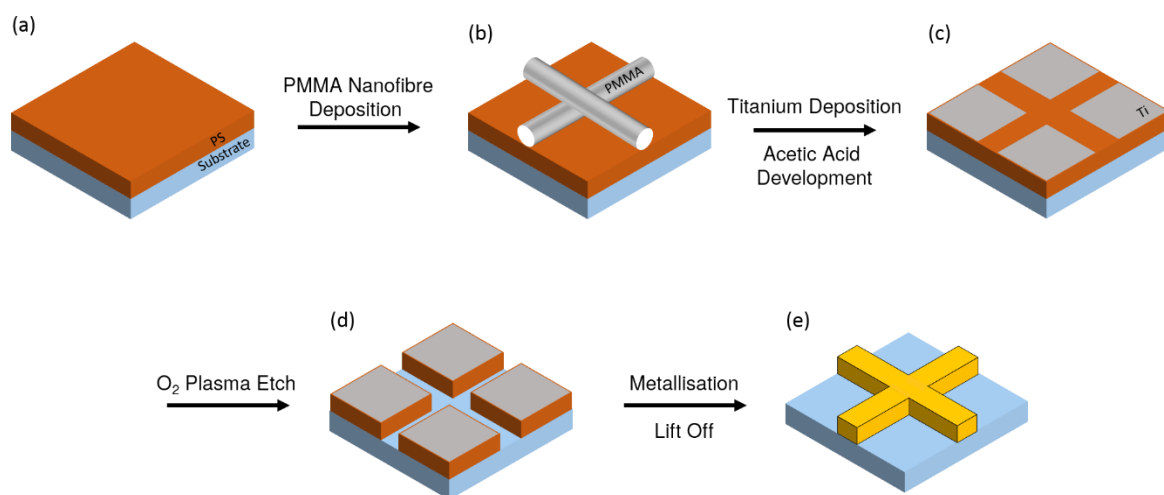


Figure 4.1. Schematic overview of main steps involved in the polymer nanofibre templating process. (a) PS film coated substrate (b) PMMA nanofibres deposited on PS layer (c) Developed Ti-PS pattern (d) Oxygen plasma etched Ti-PS pattern (e) Seamless metal nanowire network.

4.2.1 Nanofibre Templating

This section describes a pattern transfer procedure for the formation of a deposition template based off a PMMA nanofibre network. A general overview of the process is discussed and the optimisation of each process step is detailed in full.

4.2.1.1 Process Overview

Figure 4.1 details a schematic overview of the templating process developed during the course of this work to fabricate metal NWNs with seamless junctions. The process exploits the orthogonal solubilities of polymethylmethacrylate (PMMA) and polystyrene (PS) to map the nanofibre network structure onto a template which can then be used for metal deposition. Firstly, a transparent substrate was coated in a uniform layer of PS through spin coating of a toluene based solution; 300 nm film thickness was used for all samples in this work and was fabricated from a 6% (w/v) solution of 150k PS spun at 4000 rpm. The film was annealed at 130°C for 30 minutes after spin coating to smoothen any surface roughness. PMMA nanofibres were then deposited through electrospinning of a 6% (w/v) solution of 350k PMMA in DMF with the addition of 5% CTAB (w/w% with respect to PMMA).

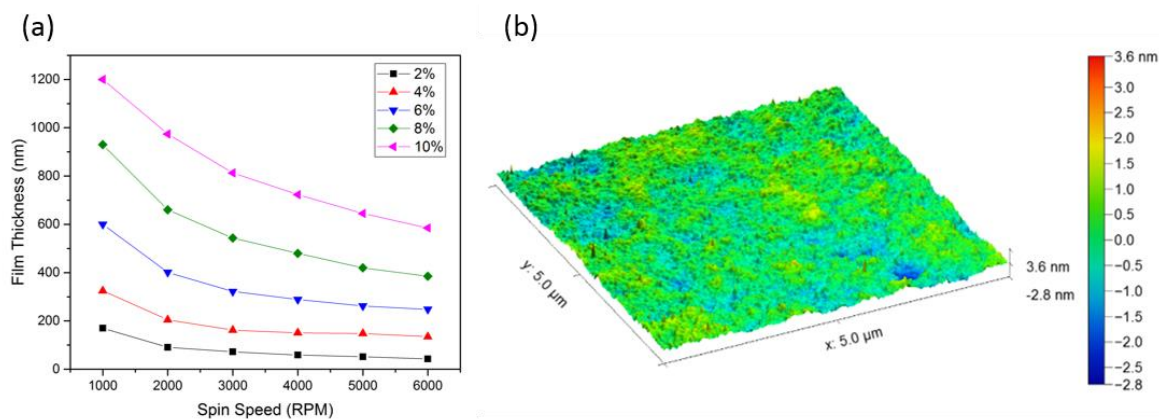


Figure 4.2. (a) Relationship between spin coating RPM and thickness of PS film for a range of toluene solutions varying between 2-10% (w/v) (b) 3D AFM topography of annealed 300nm thick PS film.

After nanofibre deposition, the substrate was annealed at 80°C for 5 minutes to soften the fibres and ensure they lay flush with the film surface. A 40 nm titanium layer was then deposited using an ebeam vacuum deposition system. The metallised substrate was then placed in glacial acetic acid and sonicated at 85 kHz at low power for 15 seconds to selectively dissolve the PMMA nanofibres without affecting the underlying PS film. The sample was then gently agitated in DI H₂O for 30 seconds to remove any stray titanium fragments. An oxygen plasma etch was performed to remove the exposed PS sections that were masked by the nanofibres during titanium deposition. Two 30 minute etches were carried out to fully expose the underlying substrate and to develop an overhang for a clean lift off. The resulting Ti-PS template structure was a negative pattern of the original PMMA nanofibre network. After an ebeam metal deposition process, an overnight lift off in chloroform revealed the final interconnected metal nanowire network with seamless junctions.

4.2.1.2 Polystyrene Spin Coating

The fabrication process begins with spin coating a layer of polystyrene on the desired substrate. Spin coating is a widely used solution based technique for the formation of polymer films. The curves shown in figure 4.2 (a) demonstrate the relationship between film thickness and spin speed for a range of PS concentrations. Solutions of higher concentrations experience stronger viscoelastic forces during the spinning process which results in thicker films.⁴² The final film thickness is also dependant on

the molecular weight of the polymer, dicarboxy terminated PS supplied by Scientific Polymers with a M_w of 150k was used for all spin coating experiments in this work. Figure 4.2 (b) shows a high resolution AFM image of the surface of a 300 nm PS film after a 30 minute anneal at 130°C. The film showed a uniform thickness across the sample area with a low RMS roughness of ~ 2 nm.

4.2.1.3 PMMA Electrospinning

As discussed in chapter 2, electrospinning is a versatile technique for the formation of uniform fibres by drawing a polymer solution through a narrow opening held at high potential. In this work networks of PMMA nanofibres were fabricated and used as a sacrificial template in a pattern transfer process. The morphology of electrospun fibres is known to depend on a large number of variables⁴³⁻⁴⁴ and this section describes the optimisation of the main electrospinning parameters for the formation of smooth continuous PMMA nanofibres.

DMF based solvent systems are generally employed for the electrospinning of PMMA,⁴⁵⁻⁴⁷ bead-free fibres have also been reported using other solvents such as THF but the fibre surfaces display a high degree of roughness.⁴⁸⁻⁴⁹ All electrospinning experiments performed during the course of this work used 350k M_w PMMA supplied by Sigma Aldrich in powder form. All solutions were prepared by stirring at 60°C overnight and were then allowed to cool to room temperature before use. The onset of jet formation was observed at 10 kV using a 12 cm tip collector distance (TCD), 1 ml/hr flow rate and a 25G stainless steel needle. Through varying the polymer concentration it was found that solutions of 10% (w/v) PMMA yielded defect free fibres with uniform diameters as shown in figure 4.3 (b). Beads appeared in the fibre structure with increasing frequency as the concentration was decreased; figure 4.3 (a) shows beaded fibres electrospun from an 8% solution. The concentration dependence of beading is a well reported phenomenon in electrospinning and is attributed to the surface tension induced Rayleigh instabilities in the fluid jet.⁵⁰⁻⁵¹ Hence for a pure DMF solvent system, the smallest diameter for a uniform PMMA fibre without beads was 1316 ± 297 nm.

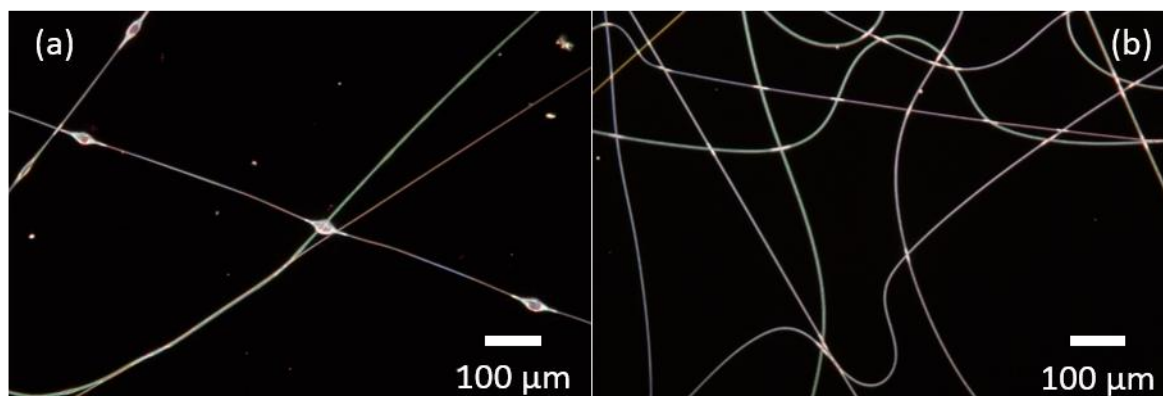


Figure 4.3. Optical dark field image of PMMA nanofibres spun from (a) 8% and (b) 10% (w/v) DMF solution.

In order to obtain narrower fibre diameters the effect of adding a surfactant, cetyltrimethylammonium bromide (CTAB), on the fibre morphology was investigated. All CTAB used in this work was $\geq 99\%$ BioXtra grade supplied by Sigma Aldrich in fine powder form. Figure 4.4 (a) shows the relationship between fibre diameter (measured from a sample of 30 fibres per test) and CTAB content for a 10% PMMA-DMF solution. A sharp decrease in the average fibre diameter is observed which levels off beyond 1% with no further change observed with increasing CTAB concentration. CTAB and other quaternary ammonium salts (QAS) have been demonstrated to strongly influence solution conductivity⁵²⁻⁵⁵. Higher conductivity results in an increased charge density of the fluid jet during the electrospinning process and thus increases the electrostatic repulsion experienced by the polymer jet driving stronger whipping instabilities and ultimately yielding narrower fibres.⁵⁶

Figure 4.4 (b) shows the relationship between average fibre diameter (measured from a sample of 30 fibres per test) and PMMA concentration for a pure DMF solvent and a 5% CTAB-DMF solvent system electrospun at 10 kV, 12 cm TCD, 18G stainless steel needle and 1ml/hr flow rate. For PMMA solutions based on pure DMF, beaded fibres were always observed from solutions of 8% concentration or less but in the case of the 5% CTAB-DMF solution, the PMMA concentration could be lowered to 4% with no observable bead defects. The distortion of the fluid jet into bead defects is driven by the actions of capillary forces acting to minimise the exposed surface area of the fluid jet. As a surfactant,

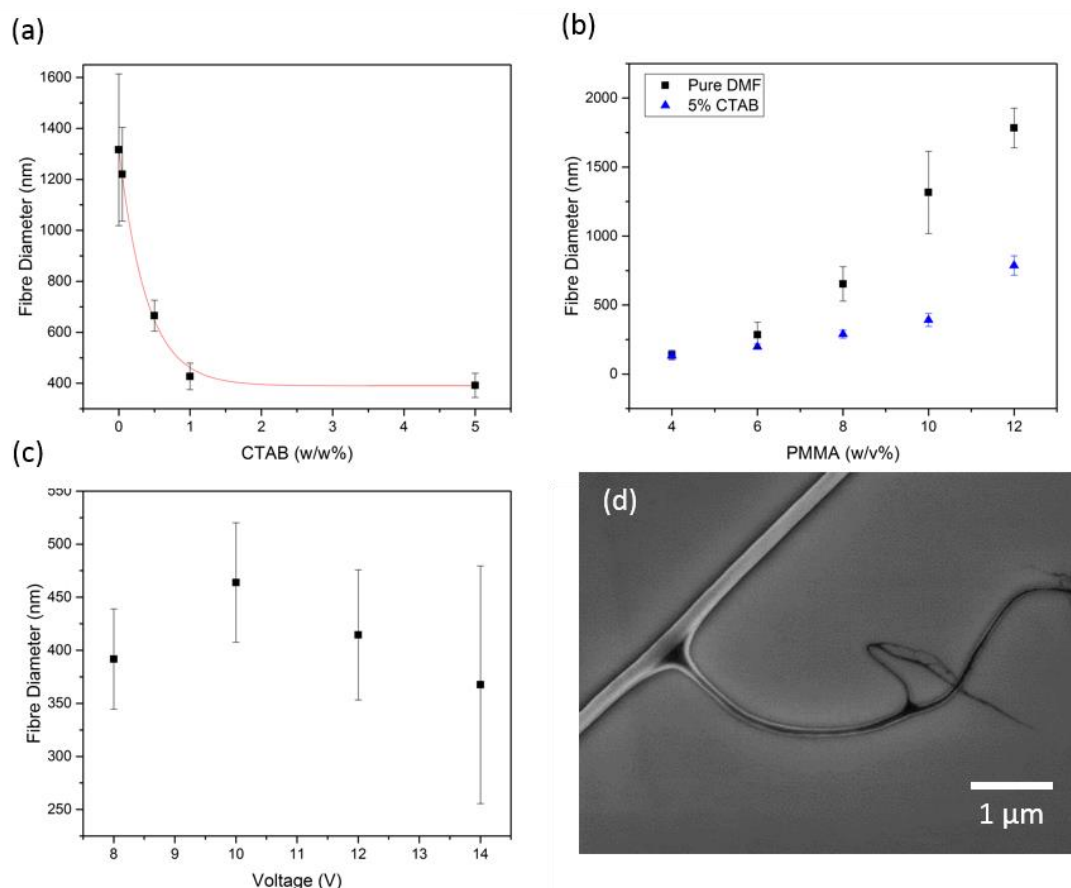


Figure 4.4. (a) Relationship between CTAB concentration and fibre diameter for a 10% PMMA DMF solution with asymptotic fit (red curve), (b) Relationship between fibre diameter and PMMA concentration for a pure DMF and 5% CTAB-DMF solvent systems, (c) Relationship between fibre diameter and applied voltage for a 10% PMMA [5% CTAB] DMF solution and (d) SEM image of branched fibre electrospun at 14 kV.

CTAB has been widely reported to decrease surface tension and hence reduce the tendency for beading.⁵⁷⁻⁵⁸ Figure 4.4 (c) illustrates the relationship between fibre diameter (measured from a sample of 30 fibres per test) and applied voltage. No significant trends are noted beyond the standard deviation widths, however there is a large increase in the diameter variance at 14 kV. This is due to the formation of smaller secondary fibres branching from the body of the primary fibre as shown in figure 4.4 (d). These branched structures have been previously reported in other polymer systems, and are likely caused by excessive charge on the fluid jet during electrospinning.⁵⁹ No branched fibre structures were observed at applied voltages below 14 kV.

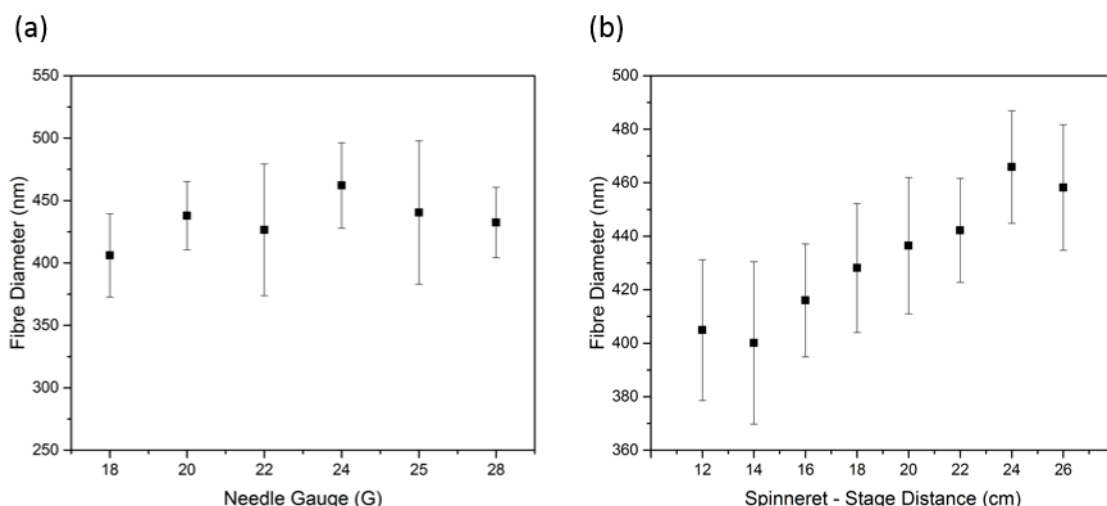


Figure 4.5. Relationship between the average fibre diameter and (a) needle gauge, and (b) TCD distance for a 10% PMMA 5% CTAB-DMF solution.

The dependence of the average fibre diameter (measured from a sample of 30 fibres per test) on tip width and TCD were also investigated as shown in figure 4.5 (a) and (b) respectively. No significant dependence on needle size was evident which is typical for polymer electrospinning.⁶⁰ A minor trend of increasing average fibre diameter with increasing TCD was noted and attributed to the weaker field strength as the distance from the tip to ground was increased.⁶¹ No other change in fibre morphology was observed while varying either of these parameters. The effect of flow rate on the spinning process was also examined; at rates below 1 ml/hr, the hanging droplet present at the tip was seen to rapidly deplete upon the onset of electrospinning. Fibre formation then halted until additional solution built up a new droplet resulting in a staggered spinning process with fibres depositing in regular bursts. At rates above 1 ml/hr, continuous fibre formation was observed but excess solution accumulated at the tip leading to frequent drops falling on the sample underneath. A flow rate of 1 ml/hr provided enough solution to prevent depletion of the droplet while minimising excess drops.

From the results of these optimisation experiments a set of electrospinning conditions was established and used in combination with a CTAB-DMF solvent system to give a tuneable process for the production of PMMA nanofibres. All electrospinning performed in this work used an applied voltage of 8 kV, 1 ml/hr flow rate, 12 cm

PMMA (w/v) %	Mean fibre diameter (nm) $\pm \sigma$
4	133 $\pm$ 27
6	198 $\pm$ 26
8	289 $\pm$ 29
10	392 $\pm$ 47
12	787 $\pm$ 71

Table 4.1. Average diameters and standard deviations (measured from a sample of 30 fibres per test) of PMMA nanofibres fabricated using a 5% CTAB-DMF solvent system.

TCD and an 18G flat tip stainless steel needle. Table 1 details the average fibre diameters obtained using this set of parameters and shows the wide range of diameters with narrow distributions that could be accessed by varying the concentration of PMMA. All electrospinning was performed in an environmentally controlled lab at a 21°C and 50% relative humidity.

4.2.1.3.1 Collector Stage Design

The overall structure of the nanofibre network was found to strongly depend on the geometry of the collector stage. Figure 4.6 details the four types of stage designs investigated in this work. The simplest stage geometry was a flat metal plate collector and yielded a mixture of straight and regularly oscillating nanofibres as shown in figure 4.6 (a), the amplitude of the oscillation was seen to fade along the length of the fibre eventually disappearing altogether. Sinusoidally structured fibres have previously been observed in other polymer systems⁶² and it has been suggested that this unusual morphology is the result of the onset of a transient bending instability in the fluid jet during its flight which then freezes in place as the fibre solidifies and deposits on the collector.⁶³

Figure 4.6 (b) details another commonly used stage design known as a ring collector, it consists of a grounded copper ring on an insulating base with the sample placed at the centre of the ring. Fibres deposited on the ring itself are structured similarly to

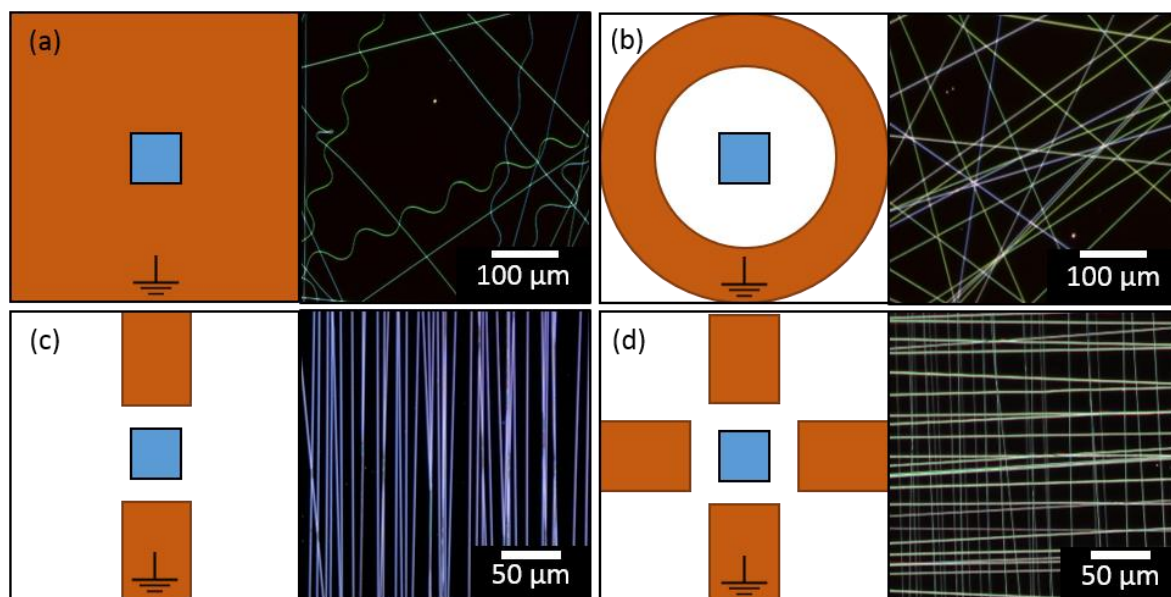


Figure 4.6. A schematic top down view of the (a) Plate, (b) Ring, (c) Parallel strip and (d) Cross strip stage geometries and the fibre network morphology formed from each. The copper and white regions correspond to grounded metal structures and insulating Teflon plates respectively; the blue square designates the position of the sample.

those deposited on the previously described plate collector. Within the central region of the ring however, the oscillations in fibre shape are no longer present and only randomly oriented linear fibres are observed. As the charged fluid jet approaches the collector, it preferentially deposits on the grounded ring structure and avoids the insulating central region. However the chaotic flight path of the jet inevitably directs some fibres toward the centre of the ring and attractive electrostatic forces influence the jet to reach across to the grounded ring edge. This additional force stretches out any residual bending instabilities in the jet structure resulting in straight fibres.⁶⁴ A similar effect is observed when using parallel strip or cross strip stage designs as shown in figure 4.6 (c) and (d) respectively.⁶⁵

Figure 4.7 (a) and (b) show fibre angle histograms measured from networks fabricated using a plate and ring collector respectively. A random angle distribution is observed in both cases with calculated averages and standard deviations closely approximating expected random average angle values of $90^\circ \pm 45^\circ$. Fibre angle analysis of a network fabricated from a parallel strip stage shows a sharp distribution centred at $90^\circ \pm 1.6^\circ$ as shown in figure 4.7 (c). A bimodal distribution was observed

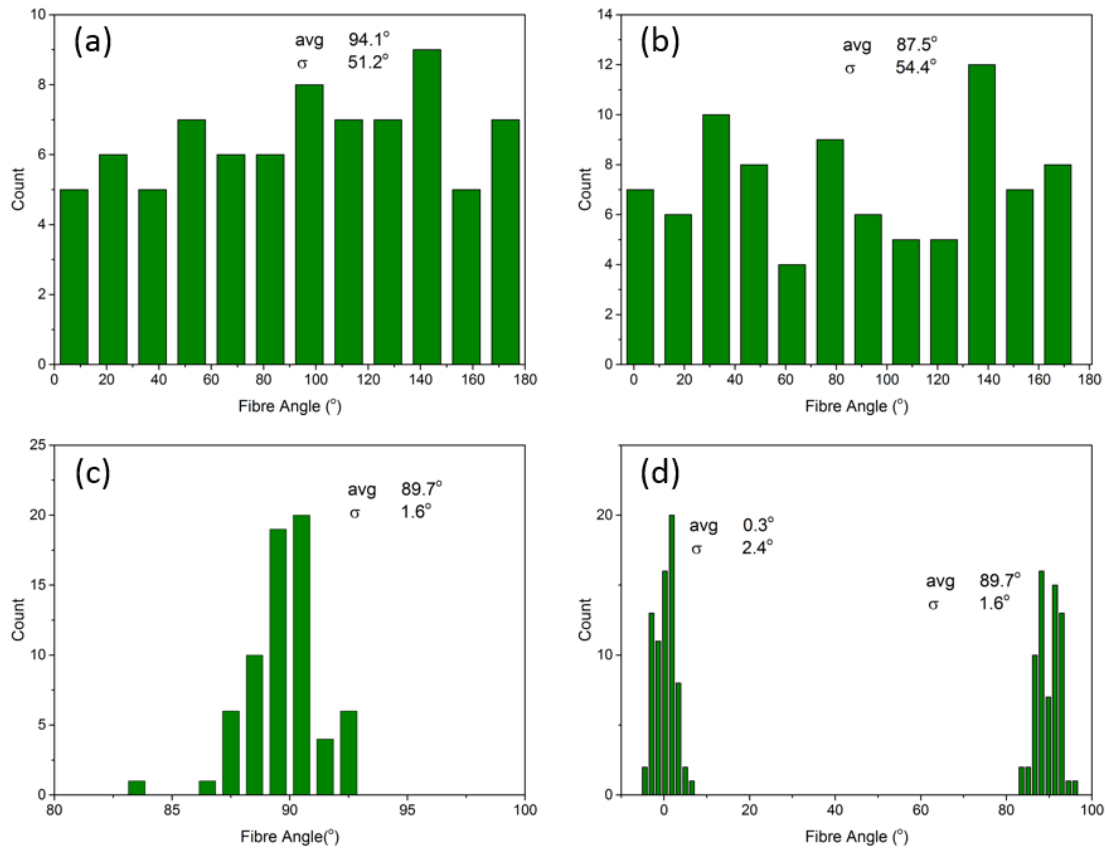


Figure 4.7. Angle frequency distributions (measured from a sample of 80 fibres) for fibre networks deposited on (a) Plate, (b) 2 cm inner diameter ring, (c) Parallel strip and (d) Cross strip stage geometries with a 1 cm gap.

in the angle distribution measured from a cross strip fabricated network as shown in figure 4.7 (d); two distinct fibre populations can be seen centred at $0.3^\circ \pm 2.4^\circ$ and $89.7^\circ \pm 1.6^\circ$ corresponding to horizontal and vertical fibres respectively. Due to the rapid rate of deposition and poor reproducibility of fibre density between samples, the parallel and cross strip stage designs were not utilised further in this work. Both the plate and ring collectors demonstrated a relatively slow deposition rate allowing for control over the area coverage by varying the electrospinning process time which is demonstrated in figure 4.8.

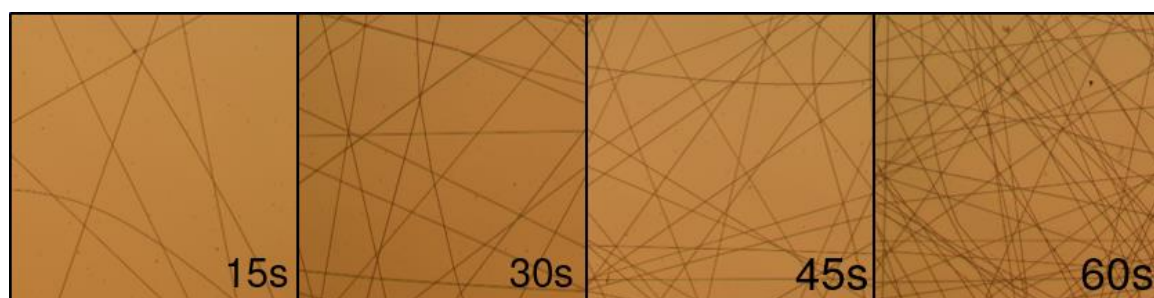


Figure 4.8. Optical bright field images of fibre networks formed over various deposition times using a ring collector.

4.2.1.4 Nanofibre Pattern Transfer

Once the PMMA NFN was deposited on the substrate, the next step in the template formation procedure was to transfer the pattern of the NFN structure onto the underlying PS film. This was performed through the deposition of a 40 nm titanium layer in an ebeam vacuum system; as shown in figure 4.9 (a), the exposed areas of the PS film were evenly coated in titanium and the nanofibres acted as masks during the deposition. The metallised sample was then sonicated in glacial acetic acid at 85 kHz at low power for 15 seconds and then lightly agitated in DI H₂O for 30 seconds, this treatment removed the titanium coated PMMA nanofibres and resulted in negative pattern of the original NFN structure. This development process exploits the orthogonal solubilities of PS and PMMA; acetic acid is an excellent solvent for PMMA and a nonsolvent for PS and so readily dissolves the nanofibres while leaving the patterned film intact.⁶⁶

At some fibre junctions, titanium was observed to have partially deposited underneath the edges of the nanofibre resulting in the narrowed structure shown in figure 4.9 (b). This was only seen in a small percentage of cases and the template width always returned to match the original fibre diameter within a micron. A potential cause for this behaviour is the suspension of weakly adhered fibres above the surface of the film from residual static charge which would allow the metal vapour cloud to partially diffuse under the fibre edges during deposition. In order to prevent these defects, annealing experiments were carried out on samples before performing metal deposition in an attempt to improve fibre adhesion. Figure 4.9 (d)

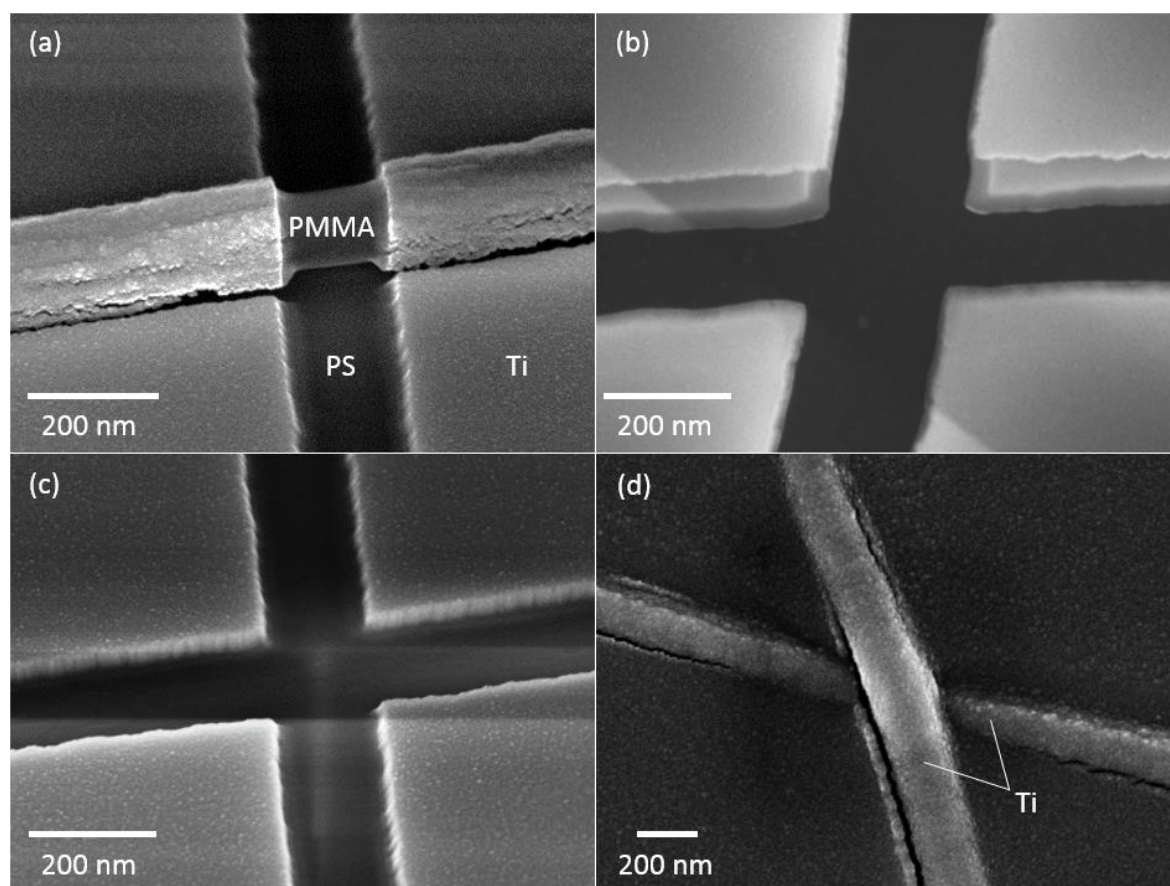


Figure 4.9. (a) SEM image of PMMA nanofibre on PS film after Ti deposition (overlying fibre at junction lifted out of view due to charging), (b) Developed Ti-PS template without annealing, (c) annealed at 80°C for 5 min and (d) annealed at 100°C for 5 min.

shows the result of a 5 minute anneal at 100°C, the PMMA fibres have visibly sunk into the underlying PS film and the development process failed due to the conformal nature of the titanium film. This sinking phenomena has previously been reported in annealing experiments performed on PS nanofibres deposited on PMMA films and is driven by surface energy interactions between the two polymers.⁶⁷⁻⁶⁸ Figure 4.9 (c) shows an ideal Ti-PS junction geometry obtained from a sample annealed at 80°C for 5 minutes after fibre deposition. No necking defects were observed at any other junctions imaged on this sample and so these annealing conditions were used for all further samples in this work.

4.2.1.5 Oxygen Plasma Etching

Following the development of the Ti-PS pattern, the final step in the formation of the deposition template structure was the etching of the uncoated PS areas to expose the

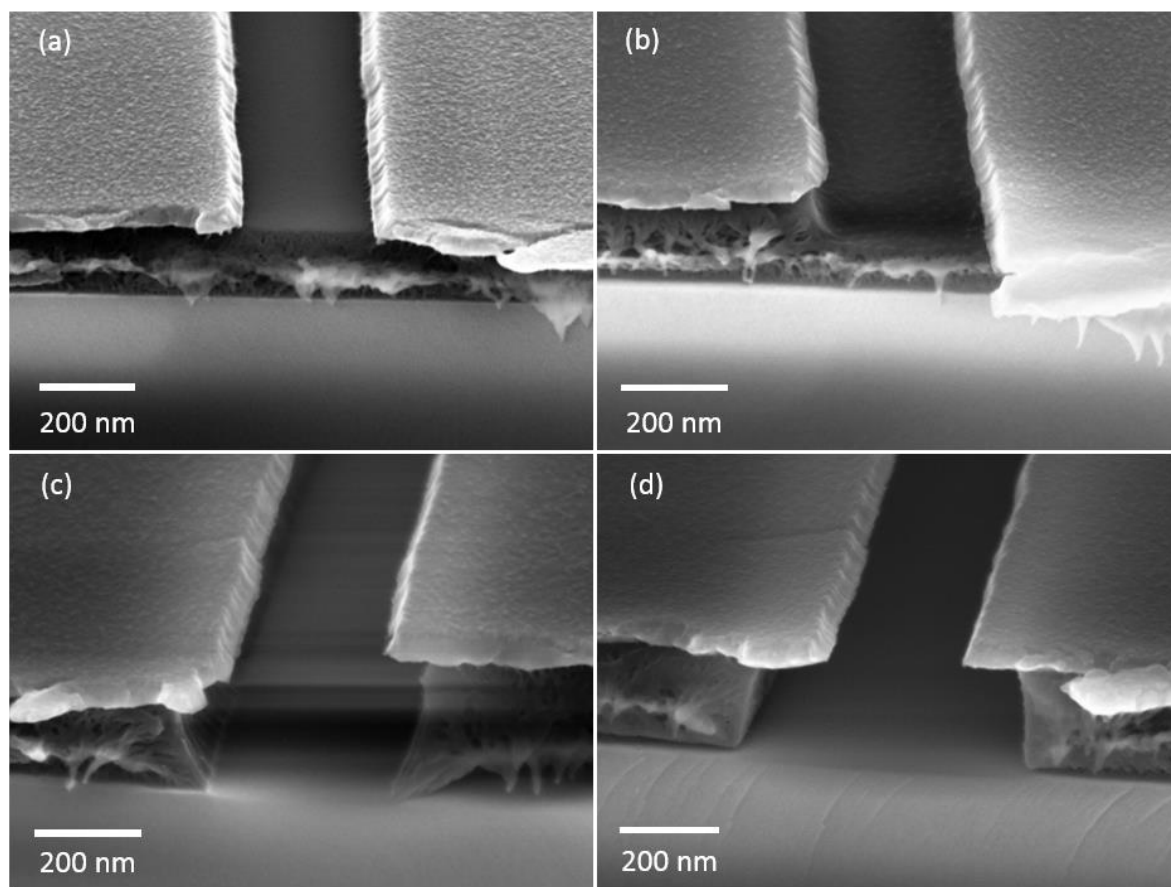


Figure 4.10. (a) Unetched Ti-PS template edge immediately after development, (b) Ti-PS template after 15 min etch, (c) 30 min etch and (d) two 30 min etches in oxygen plasma.

underlying substrate. An oxygen plasma etching process was selected for this purpose using a Diener Pico Plasma System with an O_2 pressure of 0.23 Torr and a RF power of 50 W. The highly reactive oxygen ions and radical species generated within the plasma reacted with the exposed PS to form volatile carbon oxides and water which were then pumped out of the chamber.⁶⁹ A polystyrene etch rate of 10 nm/min was achieved and the passivation of the titanium to its non-volatile oxides allowed for a highly selective etch and no mask deterioration was observed over any etch time investigated.

Figure 4.10 (a) shows a high angle SEM image of an unetched Ti-PS template with a nanofibre patterned trench visible perpendicular to the sample edge. After a 15 minute etch time, the initial removal of PS within the trench is evident as shown in figure 4.10 (b). After 30 minutes, the PS was found to be etched down to the

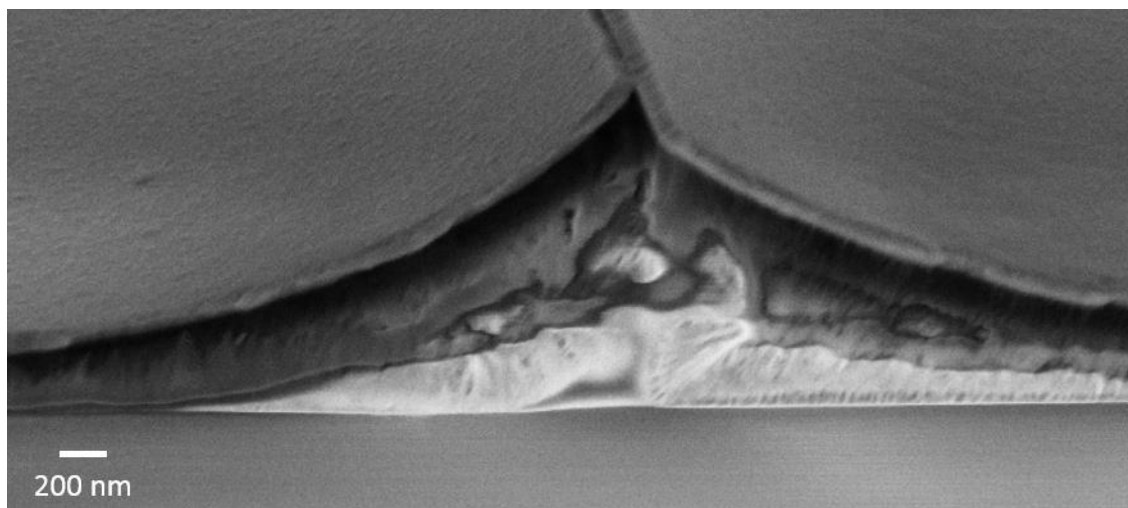


Figure 4.11. Damaged Ti-PS template after an uninterrupted 60 min oxygen plasma etch treatment.

underlying substrate as shown in figure 4.10 (c). An additional 30 minute etch resulted in the formation of a significant undercut of the PS film. The presence of an undercut is a desirable trait for deposition templates as it prevents any contact between the mask and the deposited material allowing for a clean lift off.⁷⁰⁻⁷¹

Figure 4.11 shows a SEM image of a template after a single, uninterrupted 60 minute etch, where clear damage to the template and a loss of the pattern structure was observed. During etching, the continuous bombardment of the sample by ions generates heat and the low glass transition temperature of polystyrene (97°C) makes the template susceptible to damage at elevated temperatures.⁷²⁻⁷³ An intact Ti-PS structure with a prominent overhang could be fabricated by dividing the oxygen plasma process into two 30 minute etches separated by a 5 minute cool down period.

4.2.1.6 Pattern Transfer Fidelity

Analysis of the templated structures was performed and compared against the original nanofibres in order to determine the accuracy of the pattern transfer process. Figure 4.12 (a) and (c) are SEM images of two overlapping PMMA nanofibres and a junction between two templated aluminium nanowires respectively. In the case of the nanofibre junction, one fibre is raised above the other at the point of overlap while the templated nanowires are connected by a continuous in-plane junction. The titanium deposition is performed normal to the substrate which effectively results in

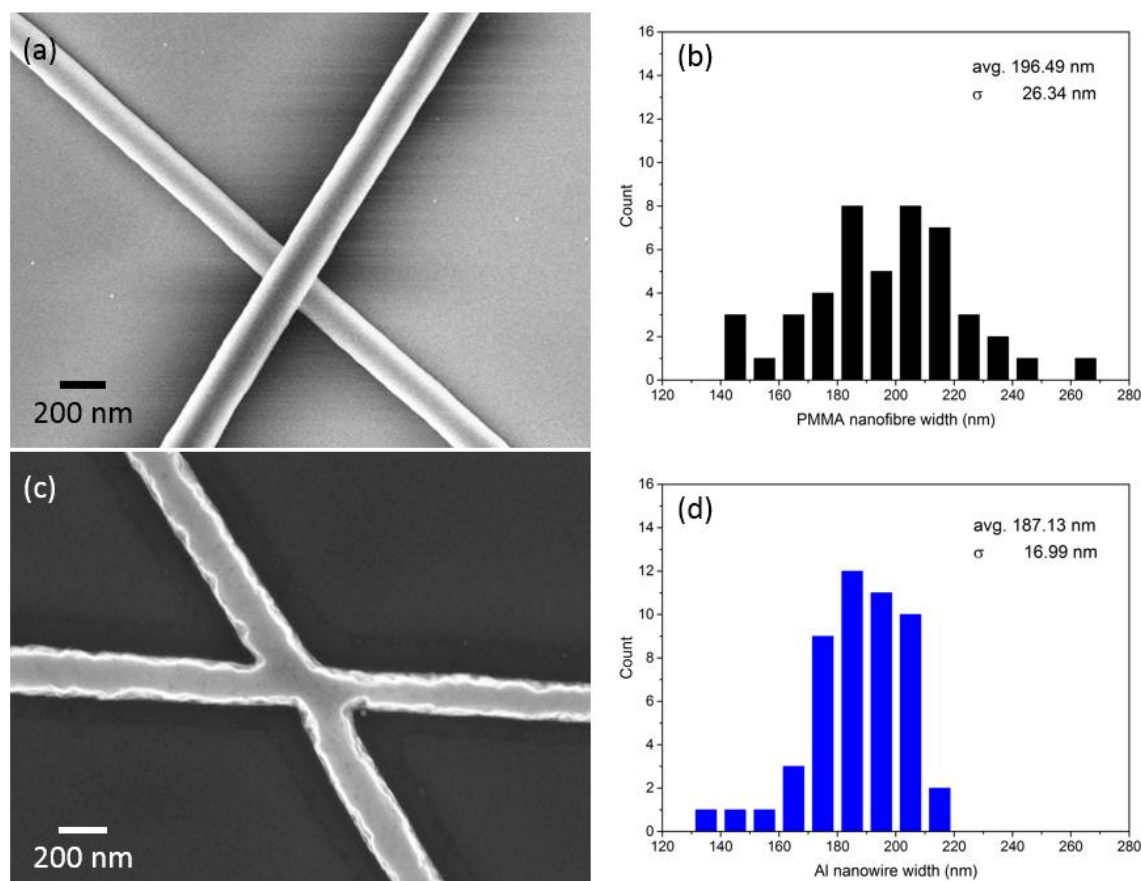


Figure 4.12. (a) SEM image of a junction between two PMMA nanofibres and (b) diameter distribution of electrospun nanofibres from a 6% PMMA [5% CTAB] DMF solution (measured from a sample of 50 fibres and 50 wires), (c) SEM image of a templated aluminium nanowire junction and (d) Width distribution of Al nanowires templated from nanofibres fabricated from 6% PMMA [5% CTAB] DMF solution.

the formation of a top down 2 dimensional projection of the NFN structure, hence the junctions are mapped down the same as any other section of the network. Figure 4.12 (b) and (d) detail histograms of the widths measured from PMMA nanofibres and corresponding templated aluminium nanowire widths respectively. No significant difference was noted between the two populations indicating that the transfer process is faithful to the original nanofibre structure.

Another important factor to be considered in a lithography process is the proximity effect, which refers to the dependence of a features definition or size on the adjacency of neighbouring structures.⁷⁴⁻⁷⁵ In the case of this nanofibre lithography process, a

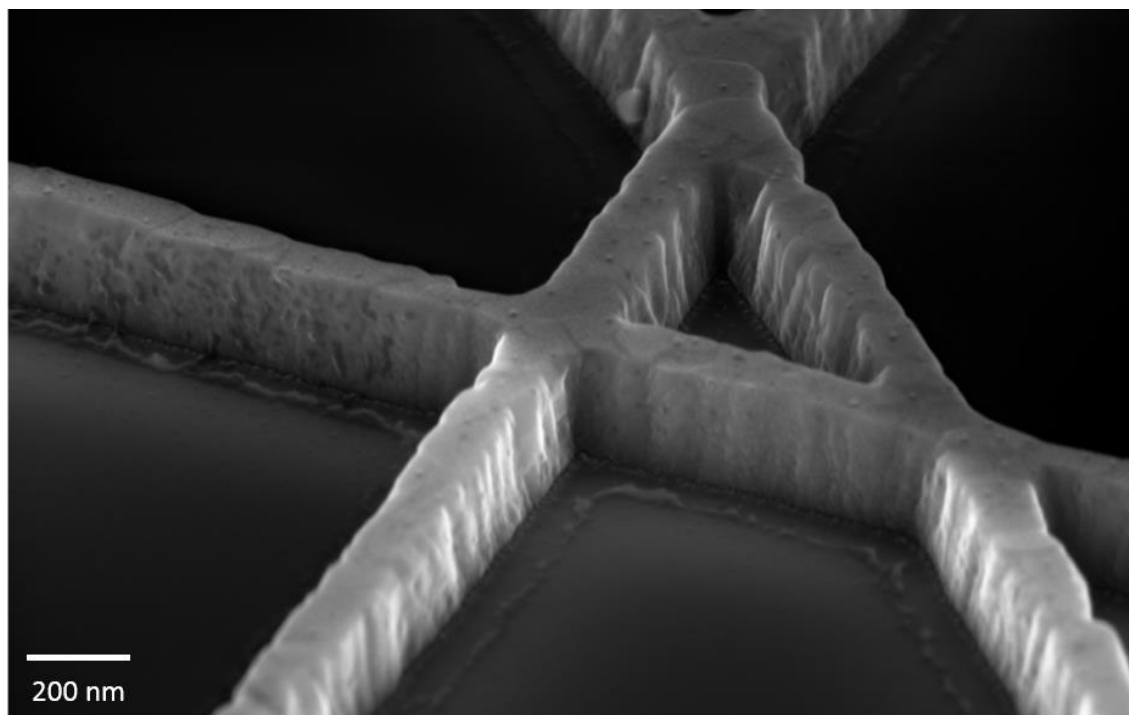


Figure 4.13. High Resolution SEM image of three templated Al nanowires in close proximity.

minimal effect was observed at the densities of nanowires investigated. Figure 4.13 shows a high resolution SEM image of three patterned aluminium nanowires in close proximity and each structure remains well defined although a slight softening of the low angle junction at the bottom right of the image is noted.

4.2.2 Aluminium Nanowire Networks

This section details the performance of aluminium nanowire networks, fabricated using the previously described nanofibre templating technique, as transparent conductors. The optimisation of an aluminium ebeam PVD process is studied and the results of measurements carried out on individually contacted nanowires are examined. A materials by design approach for transparent conductors using this nanofibre templating method is also discussed.

4.2.2.1 Aluminium Deposition

A template patterned from PMMA nanofibres with an average diameter of 450 nm was fabricated and 50 nm aluminium was deposited at a rate of 1 Å/s using a

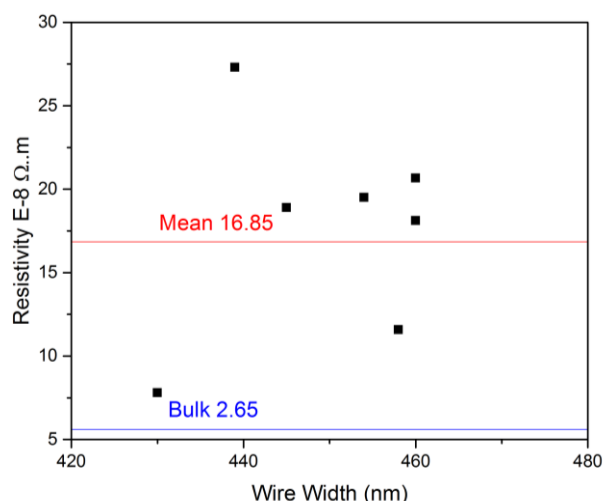


Figure 4.14. Calculated resistivities measured from 7 individual 50 nm thick Al nanowires using a four point probe technique.

Temescal FC-2000 ebeam vacuum deposition system. After lift-off, a regularly spaced square array of 50 μm pads were patterned over the network using UV lithography as shown in figure 4.16 (a). Linear wires which lay over four consecutive pads were located and their resistances measured using a four point probe technique. Alignment index marks were used to locate the wires in SEM and their precise dimensions were measured allowing for resistivity calculations, Figure 4.14 shows these calculated resistivities versus the width of the nanowire. Notably, the average resistivity taken from these measurements was higher than the value of bulk aluminium by more than a factor of 6.⁷⁶ While resistivity increases from surface scattering contributions in thin metal films are well documented,⁷⁷ the magnitude of the increase observed in this case and the wide variation between individual wires fabricated from a single deposition suggested a different cause.

The quality of metal films deposited using physical vapour methods depends on a number of parameters including the system vacuum pressure,⁷⁸ film thickness,⁷⁹⁻⁸⁰ substrate material⁸¹⁻⁸³ and temperature,⁸⁴ deposition rate⁸⁵ and residual gas composition.^{78, 85} Metallic aluminium is highly reactive, upon exposure to air, a 2-4 nm surface oxide layer rapidly forms and appreciable rates of oxidation have been observed even under high vacuum conditions.⁸⁶⁻⁸⁷ The base pressure of the ebeam

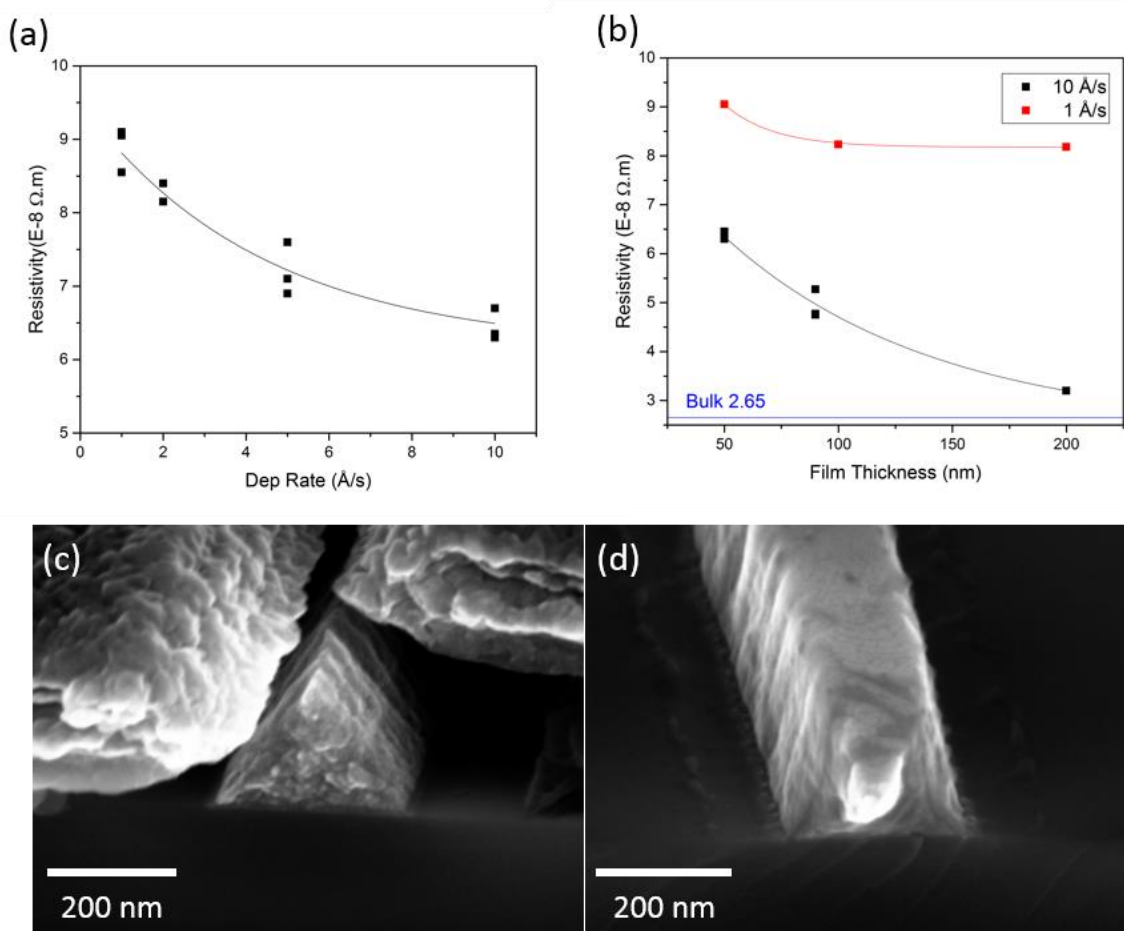


Figure 4.15. (a) Resistivity of 50 nm Al films deposited over a range of deposition rates (measured across 3 samples per run), (b) Relationship between film thickness and resistivity for Al films deposited at 1 and 10 $\text{\AA}/\text{s}$ rates (measured across 3 samples per run), cross section SEM images of aluminium nanowires deposited at (c) 1 $\text{\AA}/\text{s}$ and (d) 10 $\text{\AA}/\text{s}$.

deposition system used in this work was only on the order of $1\text{E-}6$ Torr and so oxidation during the deposition process was identified as a likely cause behind the observed resistivities.⁸⁸⁻⁸⁹ The effect of deposition rate on film resistivity was investigated by performing Van der Pauw resistance measurements on square aluminium films patterned on glass substrates using a shadow mask. Figure 4.15 (a) shows the relationship between deposition rate and resistivity for 50 nm thick Al films. A downward trend was observed with higher deposition rates resulting in material with a lower resistivity. Even at the maximum rate tested, the resistivity was still considerably higher than the bulk value so the effect of increasing the thickness of the deposited films was also studied.

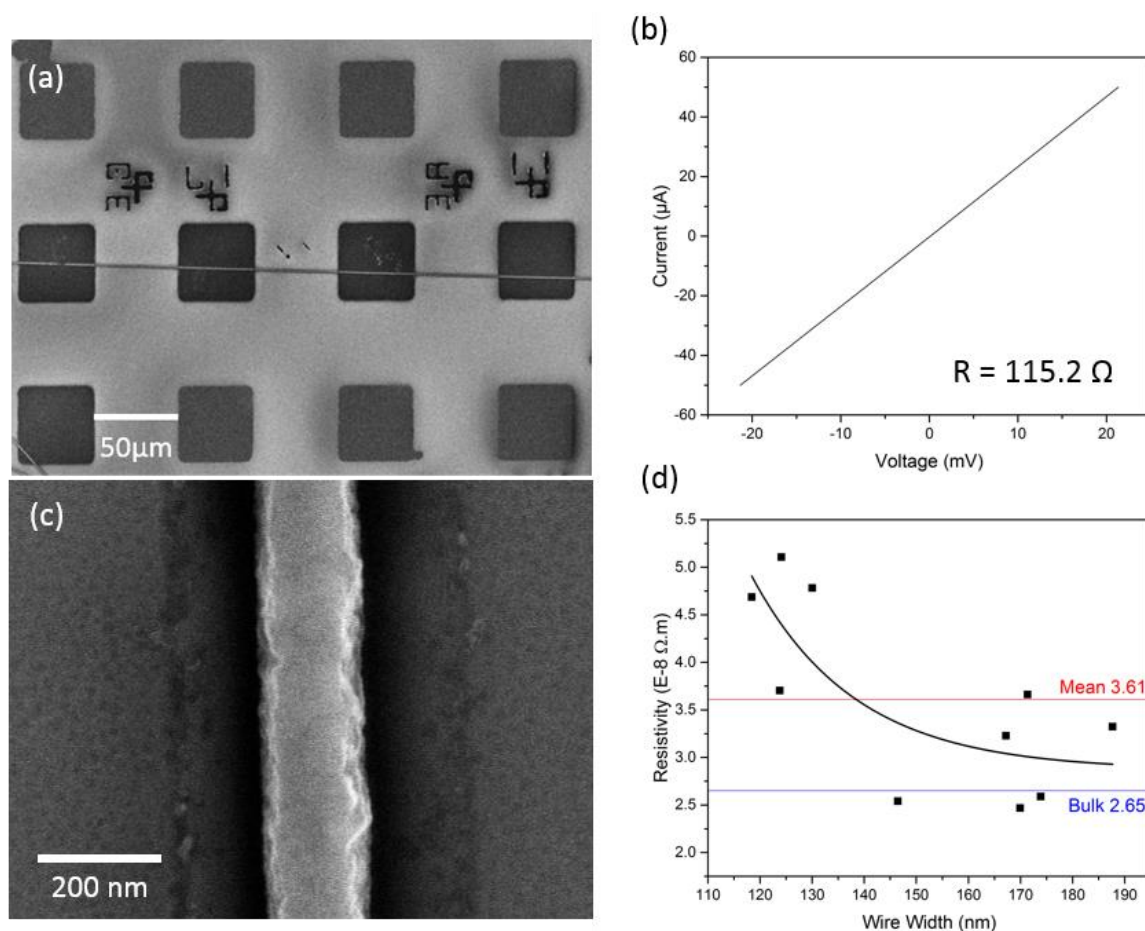


Figure 4.16. (a) SEM image of isolated individual aluminium nanowire spanning 4 collinear contact pads in square grid array, (b) four probe current-voltage graph of isolated nanowire showing ohmic behaviour, (c) high resolution top down SEM image of individual Al nanowire deposited at $10 \text{ \AA/s}$ and (d) Graph showing relationship between wire width and four probe calculated resistivities for 10 nanowires across a range of widths.

Figure 4.15 (b) shows that film resistivities close to bulk can be obtained for thick 200 nm Al films deposited at a rate of $10 \text{ \AA/s}$. A strong correlation between both deposition rate and film thickness with grain size has been reported, with increases in rate and thickness resulting in larger grains.⁹⁰ The effect of scattering at grain boundaries is therefore reduced for thicker films which also have a reduced resistance contribution from surface scattering as they have a lower surface-volume ratio. As well as these scattering based effects, the use of a higher deposition rate results in a faster rate of grain growth which outcompetes oxidation reactions from residual oxygen species present in the chamber.^{85, 91} A pronounced structural change was also noted between nanowires deposited at $1 \text{ \AA/s}$ and $10 \text{ \AA/s}$ as shown in figure

4.15 (c) and (d) respectively. A near vertical sidewall profile was observed in the case of nanowires deposited at $10 \text{ \AA/s}$, whereas this was reduced to $\sim 60^\circ$ at a rate of $1 \text{ \AA/s}$. The expansion ratio for the conversion of Al to Al_2O_3 is approximately 1.7,⁸⁶ so this tapering behaviour could be caused by the oxidation of Al that had been deposited at the template edges as the expansion of this oxide would narrow the lateral width of the template for successive aluminium deposition.

Individual resistivity measurements were repeated for Al nanowires deposited at $10 \text{ \AA/s}$ using the same UV grid pattern shown in figure 4.16 (a). Four probe voltage sweeps showed Ohmic IV behaviour at both polarities, illustrated in figure 4.16 (b). The resistivity values calculated from these wires were comparable to bulk and demonstrated a trend of increasing resistivity with decreasing wire width as shown in figure 4.16 (d). This was attributed to increased scattering from the edge roughness of the nanowires which is clearly visible in the SEM micrograph shown in figure 4.16 (c).

4.2.2.2 Transparent Conductor Performance

Following the optimisation of the aluminium deposition and characterisation of individual nanowires, the performance of Al NWNs fabricated on transparent substrates was investigated. PMMA NFNs of varying density were electrospun from 6% CTAB-DMF solutions using a disk and a plate collector stage to pattern PS coated glass and quartz substrates with linear and curvilinear wire morphologies respectively as shown in figure 4.6 (a) and (b). Deposition templates were fabricated from these networks with an average width of $187 \pm 17 \text{ nm}$ and a 190 nm layer of aluminium was deposited at $10 \text{ \AA/s}$ on each. After lift-off, a shadow mask with rows of 1 mm square contact pads was placed over the substrate and 250 nm of Al with a 5 nm Ti adhesion layer was deposited. These contact pads were used to measure the sheet resistance at multiple areas over the samples using a four point probe technique. The optical transmission was measured at adjacent areas using a Lambda 1050 spectrometer and normalised against the bare glass substrate reference transmission.

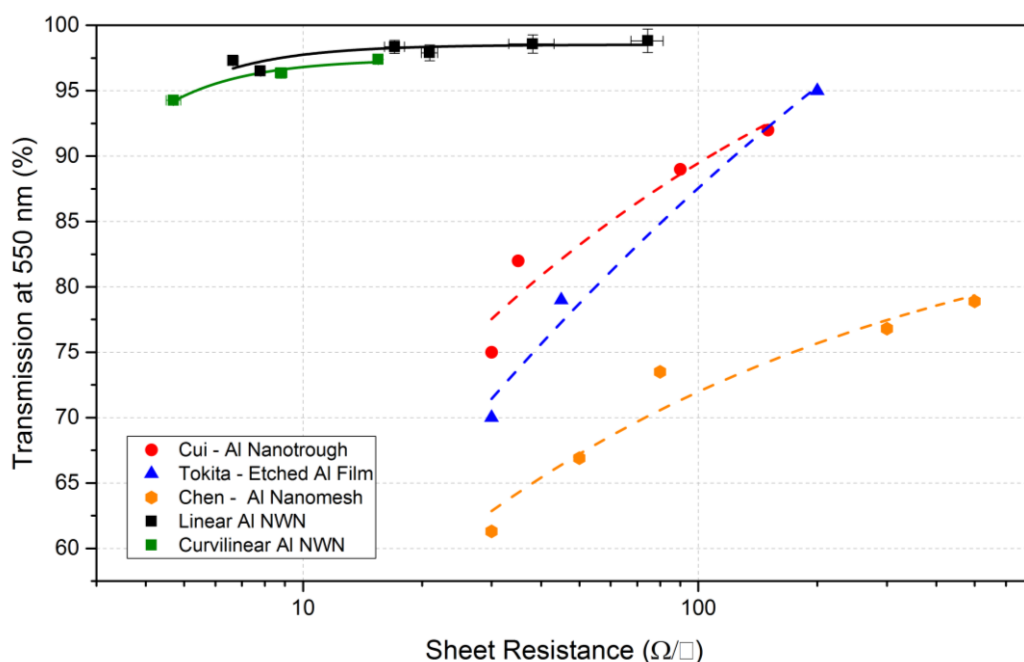


Figure 4.17. Comparison of the specular transmittance and sheet resistances measured for 190 nm thick, linear (6 networks) and curvilinear (3 networks) Al NWNs of varying density to literature publications of other aluminium nanowire based TC materials.^{34, 41, 92}

The performance of the Al NWNs fabricated from this work was compared to other aluminium nanowire based transparent conductors from literature as shown in figure 4.17. All references devices were fabricated with seamless junction geometries and both morphologies of Al NWNs considerably outperformed all other aluminium networks in terms of conductivity and transmittance. Chen *et al.* deposited an Al film on a glass substrate and performed a partial anodisation halting just after pore formation reached the underlying substrate.⁹² After etching of the oxide, a thin conductive Al film with close packed holes remained and the size of the openings was varied by extended anodisation time. Tokita *et al.* deposited a random curvilinear network of electrospun PS nanofibres onto a 50 nm Al film and after annealing to fuse the fibre junctions performed a KOH etch yielding a network of 500nm wide Al ribbons.⁴¹ Cui *et al.* also used electrospinning to fabricate a linear freestanding network of 400 nm diameter PVA nanofibres mounted on a copper ring collector, aluminium was then thermally evaporated onto this structure at a thickness of 100 nm and transferred onto a transparent substrate to give an Al nanotrough network.³⁴ The improved performance demonstrated by the Al NWNs fabricated from this work is attributed to their higher cross-sectional ratio compared to the wide and

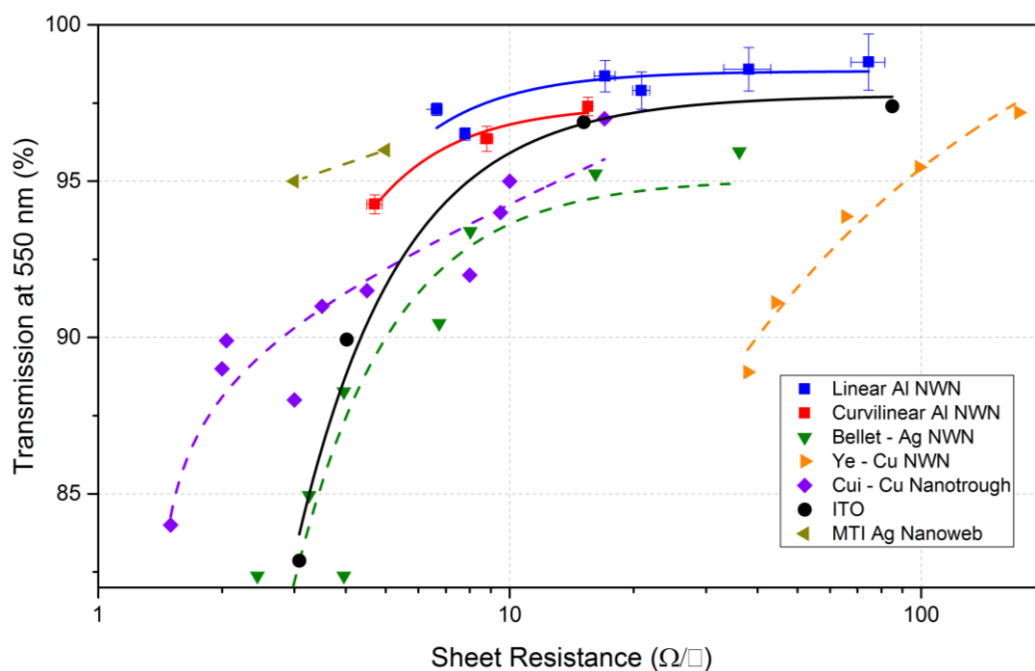


Figure 4.18. Comparison of the specular transmittance and sheet resistances of 190 nm thick linear (6 networks) and curvilinear (3 networks) Al NWNs from this work against commercial ITO films and a selection of the best performing TCs from literature references.^{34, 93-97}

thin nanostructures referenced, i.e. a greater thickness of aluminium was present for the same area coverage. Additionally, the quality of evaporated metal films depends heavily upon the type of substrate material used and Cui reported that increased resistivity values above bulk were observed for metal that was deposited directly onto polymer nanofibres.

The performance of the fabricated Al NWNs was then compared to an ITO reference and a selection of the top alternative TC materials referenced from literature as shown in figure 4.18. Both NWN morphologies rank higher than almost all other materials in this comparison, including ITO. The superior performance of these seamless aluminium networks to both silver and copper individual nanowire based devices demonstrates the importance of junction resistances between nanowires on the overall device behaviour.⁹⁸ The performance offset between the two network geometries is attributed to the increased efficiency in terms of area coverage for straight versus wavy nanowires. The difference however, is small and the fabrication of linear networks with ring collectors is restricted to small diameters which is a

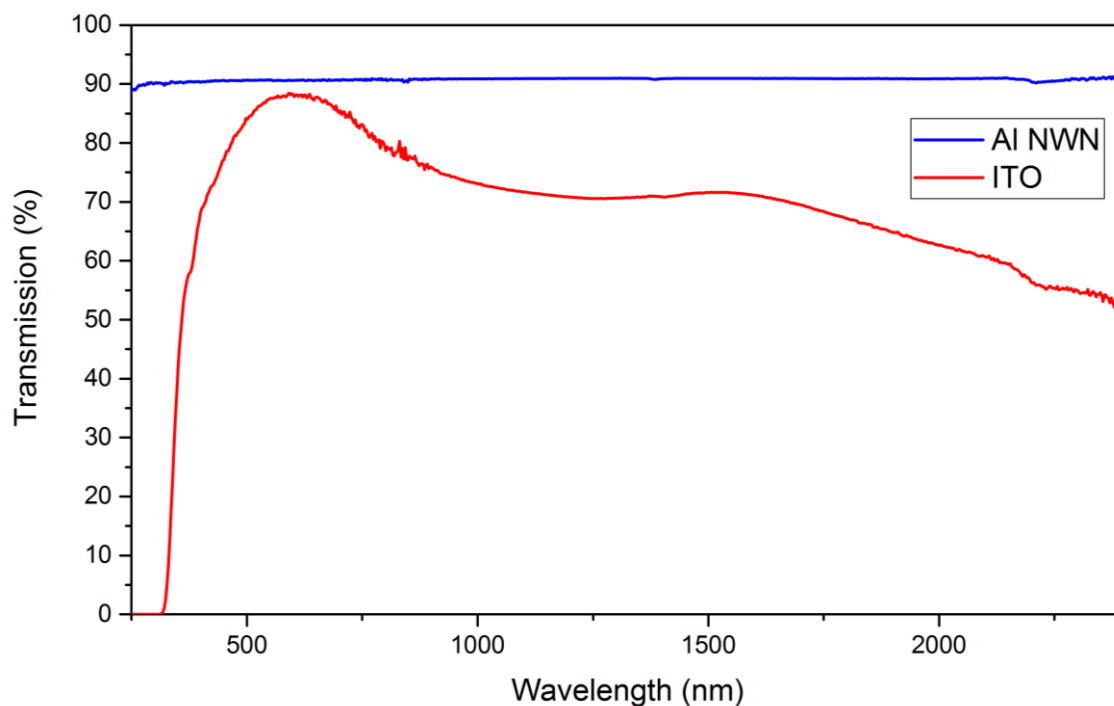


Figure 4.19. Diffuse transmission spectrum of an Al NWN (blue) and an ITO thin film (red) on quartz substrates taken from 200 nm to 2400 nm.

notable limitation of nanotrough network approaches. The simple design of the plate collector stage allows for a virtually unlimited area to be patterned using this technique, the other steps of this process; spin coating, metal deposition, and plasma etching are also highly scalable and widely used across industry. The high performance of MTIs Nanoweb technology is also worth discussing, they employ a roll to roll UV lithography fabrication technique to pattern and deposit regular hexagonal arrays of 500 nm thick and wide silver networks. The use of silver, as well as the same seamless junction geometry and high cross-sectional ratios present in the nanofibre templated structures from this work, explains the exceptional performance of MTIs Nanoweb devices.

For certain applications such as solar cells, the TC transmittance outside the visible wavelength range can have an important impact on device performance. To investigate the transparency of the Al NWNs in the UV and IR ranges, devices were fabricated on quartz substrates using a plate collector stage and compared against a quartz mounted ITO film. As shown in figure 4.19, ITO exhibits a sharp decrease in transmittance below 300 nm corresponding to its direct band gap of 4 eV and a

gradual decrease is also observed into the IR region which is attributed to the doping dependant plasma resonant wavelength of ITO.^{14, 99-100} The transmission of the Al NWNs was observed to be uniform across all wavelengths tested from 200 nm up to 2400 nm. As a metal, aluminium displays minimal absorption at most wavelengths and while transmission can occur at appreciable levels through thin metal films it can be considered as negligible for these 190 nm thick nanowires.^{66, 101} The featureless transmission spectra can be attributed to the reflectance coefficient of aluminium which is relatively constant over a wide range of wavelengths.¹⁰²⁻¹⁰³

4.2.2.3 Materials by Design and Device Stability

There exists a wide range of applications that utilise TC coatings and each has their own particular requirements in terms of transmission and sheet resistance values. For this reason, an ideal TC fabrication process should enable a materials by design approach, where the device properties can be modified and customised to match the needs of the intended application. The sheet resistance of an ITO film can be easily controlled by varying the film thickness during deposition, a process feature which, in combination with ITOs high visible light transparency, has resulted in its dominant market position. The sheet resistance of silver NWNs can also be tuned by varying the density of nanowires applied during the coating process, the diameter of the wires used also affects the final value of sheet resistance.

Figure 4.20 (a) illustrates the performance of 190 nm, 80 nm, and 40 nm thick aluminium curvilinear NWN devices with varying nanowire area densities. As expected for lower deposition thicknesses, the sheet resistance was observed to shift to higher values while the transmission remained unaffected. This effect is highlighted in figure 4.20 (b) which compares three networks of each with 97.4% transmittance but with Al thicknesses of 190 nm, 80 nm and 40 nm. Previous work published on metal grids typically report decreased transmission values as wire thickness increases due to increases scattering losses,¹⁰⁴ however these are measured across a height range of microns which is an order of magnitude larger than the scale examined in this work. This result demonstrates the versatility of this fabrication technique for the production of TC materials with tuneable properties. The

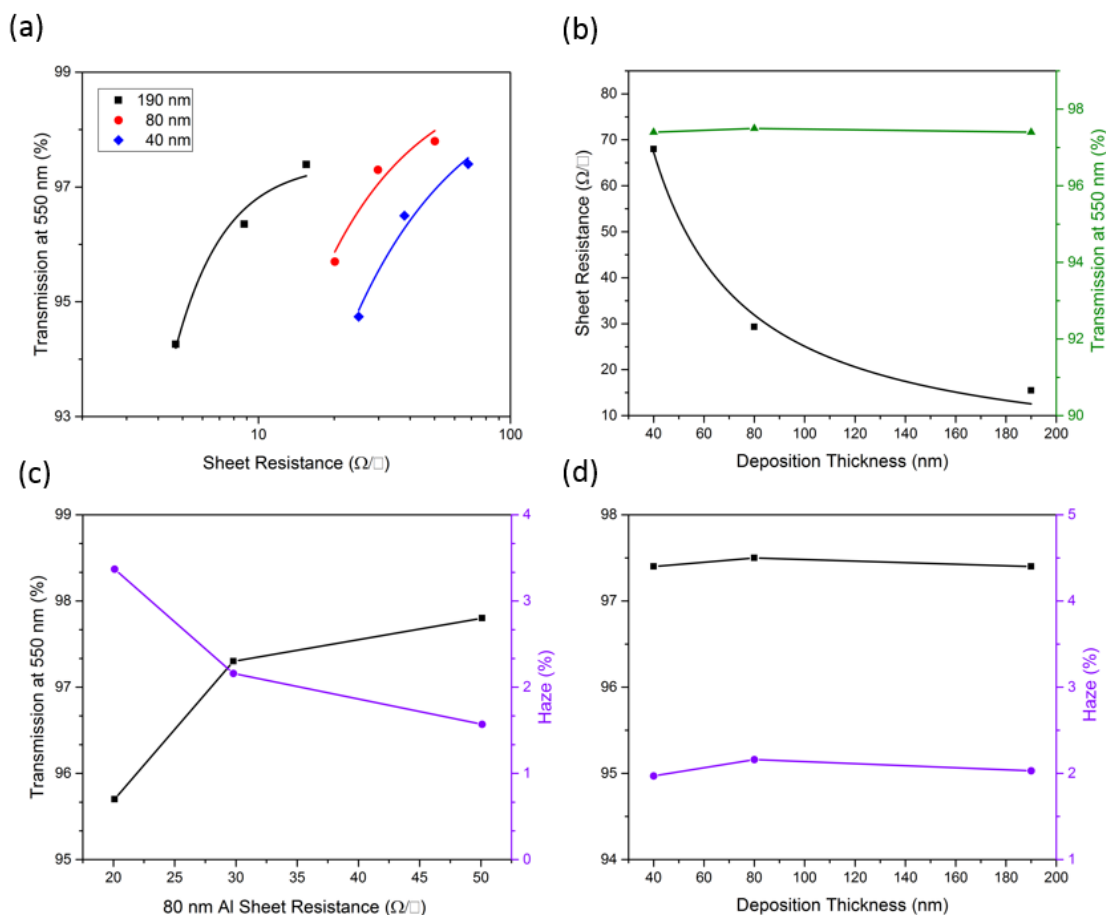


Figure 4.20. (a) Plot of transmission versus sheet resistance of 9 curvilinear Al NWNs of varying thicknesses (b) Relationship between deposition thickness and sheet resistance measured for 3 networks with 97.4% transmittance, (c) Dependence of transmission and haze on nanowire density (approximated by sheet resistance) for 3 networks 100 nm thick and (d) Graph of dependence of transmission and haze on deposition thickness for 3 networks.

transmission of the device is directly proportional to the density of nanofibres which can easily be controlled by the duration of electrospinning time, the sheet resistance can then be set to the desired value by the thickness of aluminium deposited. This design strategy separates the properties of transparency and sheet resistance allowing for total control over the device behaviour. In addition to a high ratio of transparency to conductivity, the haze of a TC material is another important figure of merit. Haze is defined as the ratio of a materials specular to its diffuse transmission and quantifies the amount of light that undergoes forward scattering. Figure 4.20 (c) graphs the relationship between sheet resistance and transmission and haze, shown as black and purple curves respectively, for 100 nm thick Al networks. As the height

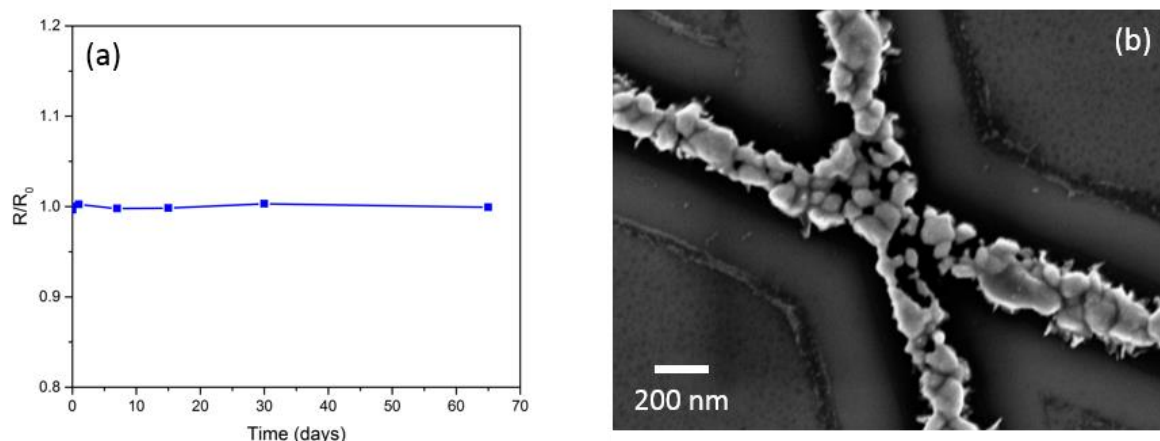


Figure 4.21. (a) Resistance of an Al NWN device measured over 65 days left in ambient conditions (b) Sulfurised silver NWN exposed to ambient conditions for 2 hours after template lift-off.

of the wires is uniform across the sample, sheet resistance can be used as a proxy for area coverage of the substrate with lower sheet resistances corresponding to greater density of nanowires. As expected, the device transmission is reduced and haze is increased for denser network. Figure 4.20 (d) demonstrates that as in the case of transmission, the haze of the device is also independent of the thickness of aluminium deposited. Haze is considered undesirable for touchscreen applications where it reduces image clarity but is advantageous for solar cells where scattering increases the path of the incident light leading to greater carrier generation.¹⁰⁵⁻¹⁰⁶ Typical haze values for ITO and Ag NWNs are on the order of a few percent and these Al NWNs demonstrate comparable scattering behaviour.¹⁰⁷

A significant problem associated with silver NWNs is their susceptibility to corrosion from environmental sulfur compounds. Silver does not demonstrate passivating behaviour and readily forms silver sulfide upon exposure to gaseous sulfur containing species. Figure 4.21 (a) shows the highly stable resistance of an 8.5 Ω/sq Al NWN left exposed to ambient conditions and periodically checked using a four point probe measurement over the course of two months. A seamless silver NWN was prepared in parallel with the Al sample, Figure 4.21 (b) shows an SEM image of this sample taken 2 hours after performing template lift off. The corrosion was so extensive and rapid that no reference measurements could be performed on this or any other silver sample prepared during this work. Along with the significantly lower cost, this

experiment demonstrates the corrosion resistance of aluminium as one of the many advantages of these seamless networks over silver based TCs.

4.3 Conclusion

This chapter has detailed a novel fabrication technique for the formation of a polymer based deposition template mapped from the structure of an electrospun PMMA nanofibre network. This technique exploited the orthogonal solubilities of PMMA and PS in acetic acid to realise a template which was used to fabricate seamless aluminium nanowire networks through e-beam PVD. The relationship between RPM and final film thickness was investigated for the spin coating of polystyrene-toluene solutions and a low roughness PS film could be achieved through annealing. The PMMA electrospinning process was studied and a set of optimised conditions was determined to reproducibly produce smooth bead-free nanofibre from a CTAB-DMF solvent system. The design of the collector stage was demonstrated to impact the angular alignment of the nanofibres and the network density could be controlled through the deposition time additionally a 5 minute anneal at 80°C was found to improve the adhesion of the fibres to the PS film. E-beam deposition of a 40 nm thick titanium layer and a development step in glacial acetic acid was found to selectively remove the PMMA nanofibres and revealed an exact negative pattern of the NFN structure. An oxygen plasma treatment was carried out to etch the uncoated PS areas and expose the underlying substrate surface, a further 30 minute etch undercut the template and developed a prominent overhang which was desirable for metal deposition. SEM analysis was performed on templated nanowires fabricated by e-beam metal evaporation and the average width distribution closely matched that of the original PMMA nanofibres. Furthermore, a minimal proximity effect was observed in the final network structure demonstrating the high fidelity of this pattern transfer process.

Four probe electrical measurements on individually contacted aluminium nanowires showed that the resistivity of the deposited material was significantly higher than the bulk value. It was proposed that the poor metal quality was caused by oxidation from residual chamber gases during the evaporation process; through optimisation of the

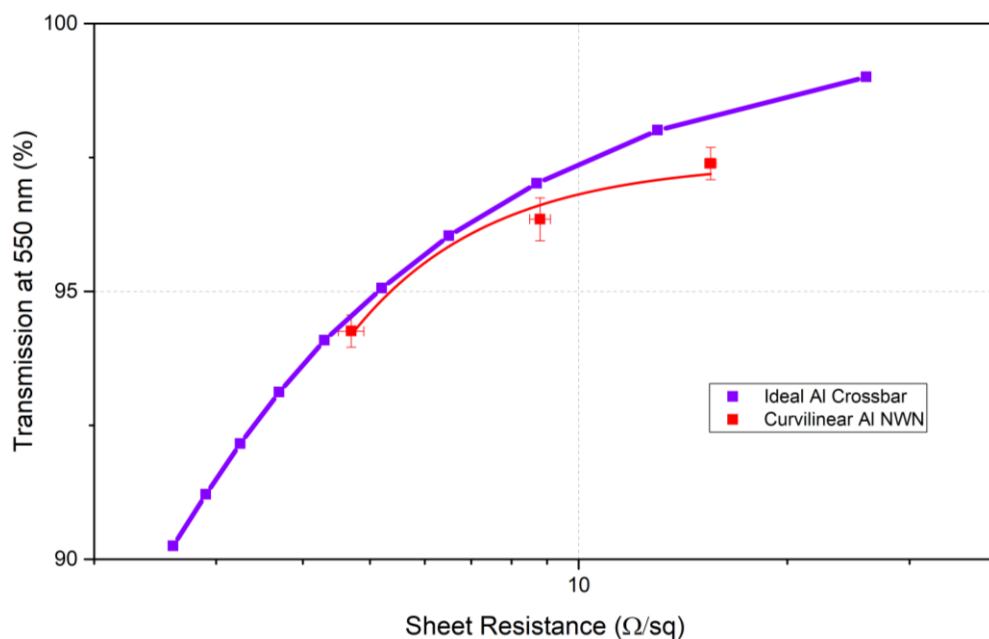


Figure 4.22. Comparison of experimental curvilinear network data to theoretical ideal aluminium crossbar array of equal thickness.

deposition rate it was found that thick films of aluminium deposited at $10 \text{ \AA/s}$ had resistivities comparable with bulk values and this was verified with additional four probe resistance measurements on individual nanowires. The spectral transmission of Al NWNS on quartz substrates was shown to be uniform across the entire wavelength range tested in contrast to an ITO/quartz reference. Optical and electrical characterisation was performed on Al NWNs templated on glass and they were demonstrated to outperform all other reported aluminium based NWNs, as well as ITO and many of the best performing TC materials from literature. Figure 4.22 shows a comparison of 3 curvilinear networks against a theoretically idealised aluminium crossbar array calculated by discounting diffraction effects and assuming bulk resistivity metal quality and 200nm wire height. It can be seen that the experimental data closely approaches the calculated curve demonstrating the highly optimised structure of these networks.

A materials by design approach was discussed with regard to the versatility of this methodology for the production of TC materials with tuneable transmission and sheet resistance values. This was demonstrated through the fabrication of Al NWNs with varying thicknesses and comparing their performance; it was illustrated that

transparency could be determined by the area density of the deposited fibres and the sheet resistance could be tailored through the thickness of metal deposited. In addition to their high conductivity/transmission figure of merit and low raw material cost, these aluminium networks also demonstrated superior corrosion stability to atmospheric sulfidation silver networks.

4.4 References

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Conclusions and Future Work

Within the setting of research laboratories, nanomaterials have been incorporated into a wide variety of technologies and have demonstrated remarkable enhancements in performance. However the commercialisation of these devices is restricted by the tedious alignment and costly patterning techniques required for their fabrication. Percolative networks of nanowires have been extensively studied in the hopes of manifesting the desirable characteristics of one dimensional materials on a more easily processed scale. The form factor of NWNs is especially well suited for applications in transparent electronics as the device behaviour can be controlled by the material composition of the nanowires and the space between wires naturally allows for optical transmission. In the case of a film based device structure, the active material must demonstrate both visible light transparency and also the desired electronic behaviour; a set of requirements which severely limits the available catalogue of materials. This decoupling of device functionality and light transmission makes NWNs a versatile tool for the design of transparent electronic systems. However, in practice NWNs rarely approach the high performance demonstrated by individual nanowire based systems due to the high contact resistances present at nanowire junctions which dominate the resistance state of the device. This junction resistance is a consequence of the minimal overlap area between intersecting wires as well as the presence of insulating passivation layers surrounding the nanowires. It is on this issue of addressing the junction limited performance of NWNs that this thesis has placed its focus. Two separate approaches were investigated for the top down fabrication of interconnected semiconducting and metallic NWNs with seamless junctions and the performance of these devices as optimal systems for transparent electronics has been examined.

In chapter 3, the fabrication of a seamless silicon nanowire network through the patterning and etching of a silicon-on-insulator substrate was described. A crack lithography process using a suspension of acrylic nanoparticles was studied for the formation of an interconnected void network and a linear relationship between the film thickness and the average template crack width was determined. Metal deposition through the crack template and a subsequent lift off step yielded a seamless Ti/Au network mounted on the silicon device layer. A single crystal interconnected silicon network was then formed through a SF_6/CHF_3 based anisotropic plasma etching process employing the metal network as an etch mask. Removal of the Ti/Au mask was accomplished through a series of selective chemical etches and SEM analysis was performed to quantify the percentage of silicon nanowires that had become isolated from the main network structure during metal etching.

A photoresist mesh with regularly spaced openings was patterned as a support structure over the silicon network and the oxide base was etched using a dilute HF solution. Gentle agitation of the substrate in an aqueous ethanol solution resulted in the detachment and suspension of the network on the surface. Transfer onto a transparent PET substrate was accomplished through slowly lifting up the PET sheet up from underneath the floating network; an acetone lift off and low temperature anneal at 80°C dissolved the photoresist support and adhered the silicon network to the new substrate. A metal assisted chemical etch process was developed to introduce discrete sections of porous silicon within the single crystal network. Au nanoparticles were fabricated through thermal dewetting of a thin gold film and were dispersed in a $\text{HF}/\text{H}_2\text{O}_2$ solution. An etch time of 1 minute resulted in a random spatial distribution of pores across the network with an average diameter of 61 ± 32 nm and an area density of $24 \mu\text{m}^{-2}$. Raman spectroscopy and TEM analysis were carried out to verify the presence of porous silicon and the intact crystalline structure of the surrounding network structure.

Metal evaporation through a shadow mask was used to deposit contact pads on the porosified network for electrical testing and the performance of the network as a

transparent photodetector was investigated. The device displayed ohmic IV behaviour during voltage sweeps and a linear photoresponse over a range of light intensities was observed under a constant applied bias. The transmission of the PET mounted network was measured to be 92% at 550 nm and remained constant across the visible spectrum. The rise and fall times of the device were measured as 0.58 ms and 1.82 ms respectively and a cut off frequency (f_{-3dB}) of 460 Hz was calculated. A trend of increasing responsivity, detectivity and EQE toward higher energy wavelengths of light was observed and the enhanced performance of a porous Si NWN was compared to an unporosified crystalline network. Low temperature electrical measurements were carried out under light and dark conditions and evidence for a variable range hopping mechanism was discussed. The observed photoconduction behaviour was attributed to charge carrier hopping between localised trap states at the porous silicon sites within the network. This device ranked among the highest performing transparent photodetectors reported from literature, and demonstrated stable behaviour during flexing tests up to a bending radius of 5 mm and over an additional 1000 bending cycles.

Chapter 4 detailed the fabrication of an interconnected aluminium NWN templated from an electrospun PMMA nanofibre network. The spin coating of polystyrene-toluene solutions was examined and a relationship between RPM and film thickness was quantified. The major electrospinning process parameters were investigated and a set of optimised conditions was determined to reproducibly fabricate smooth bead-free PMMA nanofibres from a CTAB-DMF solvent system. Randomly oriented networks of nanofibres were deposited on PS coated transparent substrates and a 5 minute anneal at 80°C was found to improve their adhesion. A negative pattern of the NFN structure was produced through the ebeam deposition of a 40 nm titanium layer over the PS mounted network. A development in glacial acetic acid was found to selectively remove the PMMA nanofibres without damaging the Ti patterned PS film. A 30 minute oxygen plasma treatment to etch the unmasked PS areas was carried out to expose the underlying substrate and an additional 30 minutes of etching resulted in the formation of an overhang suitable for metal deposition. SEM analysis of patterned aluminium nanowires fabricated by ebeam evaporation

determined that the average diameter and standard deviation of the templated structures closely matched that of the original PMMA nanofibres. Furthermore, a minimal proximity effect was observed in the final network structure demonstrating the high fidelity of this pattern transfer process and its ability to yield fully interconnected networks without any isolated sections as observed in the case of crack networks.

Four probe electrical measurements performed on individually contacted nanowires showed that the resistivity of the deposited aluminium metal was significantly higher than the bulk value. Oxidation by residual chamber gases during the evaporation process was hypothesised as the cause and optimisation of the deposition rate led to improved metal quality comparable to bulk resistivity values. The spectral transmission of Al NWNS fabricated on quartz substrates was shown to be uniform across the wavelength range from 200 nm up to 2400 nm. The performance of templated Al NWNs on glass substrates was demonstrated to surpass all other reported aluminium based NWNs, ITO and many of the best reported TC materials from literature. The versatility of this technique for the production of networks with controllable transmission and sheet resistance values was illustrated by fabricating Al NWNs with varying thicknesses and comparing their performance. In addition to their high conductivity/transmission figure of merit, these aluminium networks offer a low raw material cost and demonstrated high corrosion stability to atmospheric sulfidation.

5.1 Outlook and Future work

In this section, the impact of the results from this work are discussed with regard to the field of transparent electronics and potential areas for future investigation are suggested. This thesis has developed top down fabrication strategies utilising both film masking and etching as well as templated deposition techniques to form interconnected nanowire networks with continuous junction geometries. Seamless silicon NWNs were fabricated and characterised as transparent photodetectors; they demonstrated comparable figures of merit to the best reported devices from literature as well as stable performance under flexing tests placing them as suitable

candidates for implementation into next generation optoelectronics. PVC analysis on the networks after the titanium etching step showed a significant percentage ($\sim 33\%$) was fragmented and separated from the main network body. Investigations of milder chemical processes to remove the titanium layer,¹ or of alternative etch mask materials for patterning,² could improve the ultimate network connectivity resulting in a larger active device area and increased device performance. The transfer process to mount the network on PET presents a limit on the maximum device size that could be fabricated. Beginning the patterning process with a silicon film mounted directly on a PET substrate would remove the need for a freestanding transfer step and greatly improve the scalability of this fabrication process.³ The general strategy of patterning and etching could also be applied to films of alternate semiconducting materials (Ge, InGaAs, GaSb) to fabricate seamless NWNs with controllable wavelength sensitivity.^{4,6}

Chapter 4 describes a technique for the fabrication of a deposition template patterned from a network of electrospun PMMA nanofibres. The aluminium NWNs fabricated using this methodology have demonstrated superior conductivity/transmission ratios to many of the best performing TC materials from the literature. This high performance is accomplished through the elimination of junction resistances which offsets the lower conductivity of aluminium. The low raw material cost, corrosion resistance and tuneable device functionality of these Al NWNs places them as viable competitors to both ITO and silver NWNs. It is also important to look beyond simple figures of merit when designing TC materials for active device integration. For instance, the efficiency of solar cells is known to depend on the work function of the TC material comprising the top electrode.⁷ So in order to maximise the utility of these networks for such applications it may be necessary to deposit a top interfacial layer of a secondary metal such as nickel or gold. The implementation of these Al NWNs into functional devices as well as studies to optimise their performance are still required.

The flexibility of these Al networks has yet to be demonstrated as attempts to directly fabricate these structures on PDMS and PET substrates failed at the final chloroform

lift off step due to excessive substrate swelling.⁸⁻⁹ Optimisation of the solvent choice could lead to the successful integration of these structures on plastic substrates. Another strategy to increase the available range of substrates would be to utilise an alternative set of orthogonally soluble polymers for patterning. For example, performing the same pattern transfer methodology using PVA nanofibres on a PMMA film would allow for milder development and lift off processes in water and acetone respectively.¹⁰⁻¹¹

The ultra-high aspect ratios and controllable fibre diameters offered by electrospinning have previously been limited to only polymers or metal oxides which has restricted the potential range of device applications. This work has demonstrated a versatile technique for the scalable fabrication of seamless nanowire networks using templated PVD, which opens up a considerably greater range of potential material compositions than would be accessible through electrospinning. Combining this methodology with the patterning and etching strategy employed for the silicon crack networks further expands the available material catalogue. Investigation of networks fabricated from alternative materials would be worthwhile as a wide range of device functionalities beyond simple transparent conductors could be realised with high performance.

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