

Silver Nanowire Coatings For Electrically Conductive Textiles

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

There has been steep growth in wearable devices over the past 5 years and the ability to seamlessly integrate these devices into textiles is an exciting next step. One crucial component of achieving e-textiles is the ability of a textile to be electrically conductive for signal and power transfer. Commercially available conductive fabric typically involves metal plating, which degrades with bending and stretching. Recent alternative coatings such as polymers and carbon nanotubes have issues with low lifetimes and poor conductivity, respectively. These problems are addressed by coating fabrics and threads with networks of solution-processed silver nanowires. These silver nanowire coatings are conductive and mechanically flexible. Several deposition techniques were explored to coat fabrics including dip coating, brush coating, and transfer printing. In the latter, nanowires are printed on commercially available transfer paper coated using the Mayer rod coating technique and transferred onto different fabrics (cotton, polyester-cotton and viscose-linen). Transfer printing uses the least amount of silver nanowires compared to other coating techniques and is therefore lowest in cost. Sheet resistances in the range of 10 - 80 Ω/\square with a materials cost estimate of \$ 16 - 4/ m^2 respectively were achieved using the transfer printing technique. The transfer printing technique offers advantages including ease of application and patterning, it works for various natural and synthetic fabrics without the need for pre-treatment and it can be done at a separate time from textile fabrication. The silver nanowire coating compared to typical metal inks provide high mechanical flexibility, transparency and used less metal which results in a thinner, lighter-weight film. These silver nanowire printed fabrics are used to show three applications - an LED integrated fabric for apparel and fashion, electromagnetic interference shielding and Joule heating for thermal management. Overall, this research demonstrates an industrially compatible, printable coating process that can impart conductivity to a wide range of fabrics.

This research also designs and fabricates stretchable conductive threads. Polyester-rubber threads in a stretched-state were dip-coated with silver nanowires. After several stretching cycles, the silver nanowire coating creates a buckling pattern that helps preserve the resistance of the thread with subsequent stretching.

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Dedication

I would like to dedicate my thesis to my parents, my little sister and Adam, who have been always there as my backbone throughout and have always believed in me and my goals.

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Chapter 1

Introduction

1.1 Electronic textiles

Electronic textiles, or e-textiles, have electrical components or devices embedded into the fabric itself. The devices can include sensors, displays, and batteries. In turn, e-textiles have a wide range of applications ranging from health monitoring, sports and fitness tracking, energy storage, electromagnetic shielding, thermal management, military and construction, automotive, home technology, food packaging, and fashion. For the health monitoring area, for example, e-textiles can measure human physiological parameters like temperature, heart rate and blood pressure.

Market research shows that the smart textiles market, of which e-textiles is one major sector of, is growing fast. For example, studies have shown that the growth rate of the European smart textile market will grow over 500% between 2012 and 2020 [1]. And the American market, which occupies a large share of the smart textile market as well, is

projected be worth 1.5 billion dollars by 2020 [1].

1.2 Conductive fabric and thread

A conductive textile (fabric, thread or yarn) forms an important element in the realization of e-textiles. A conductive textile can serve multiple purposes - it can act as an interconnect between components to transfer signals or power, and it can also be used in applications on its own, like for electromagnetic interference shielding. Fabrics can be rendered conductive after their manufacture. Metal traces (silver, gold, copper, titanium, nickel) can be printed directly on the fabric surface, or metallic films can be deposited onto fabric using specialized techniques like vacuum deposition and sputtering.

1.2.1 Commercially available conductive textiles

Several companies around the world produce and supply conductive textiles. Even big retail chains like Michaels and Walmart in North America sell conductive threads and yarns. Commercially available solutions can be characterized into the four major categories of materials they are prepared with, namely: carbon fiber, conductive polymers, silver and other metals (copper, gold, tin, nickel, platinum and stainless steel). The respective companies that supply each of the conductive textiles are outlined in Table 1.1

1.2.2 Conductive thread

Regular thread can be made conductive by metallic plating, polymer or metal coatings, or by braiding a metallic wire around the thread during the thread processing. These threads

Table 1.1: Commercial conductive textiles suppliers

Materials type	Companies
Carbon fiber	Staticworx, K&K advanced textiles solutions, Kavon filter products, Marktek Inc.
Conductive polymers	Eeonyx Corporation, Polymer Science Inc., Textronics
Silver	Marktek Inc., SWIFT textile metalizing LLC, Solvay, LessEMF
Other Metals	Larid Technologies, Chromerics, Marian Inc., Kavon filter products, SWIFT textile metalizing LLC, Marktek Inc., UFP technologies, LessEMF

are then typically woven together with non-conductive threads.

Solid metal thread

Solid metal threads can be woven into fabrics directly. Or, the metallic wire can be wrapped around a non-conductive thread to provide conductivity. A third option is to have metal as the core and a non-conductive thread (eg. cotton, polyester, nylon) is spun around it. This process is called core-spinning. Lastly, one can braid the solid conductive wire made with non-conductive threads. Because of the properties of the metal wire, all these options can result in thread that is stiff, brittle and heavy.

Metal coated thread

Regular non-conductive threads can also be made conductive by coating metal onto the thread surface. Various types of thread can be coated including cotton, polyester and nylon. The different metals threads can be coated with include copper, silver, tin and nickel. These metals can either be used in their macromolecular, microparticle or nanoparticle forms. Depending on the type of coating, ink, and method used, the metallic coatings have variation in uniformity, density and post processing characteristics like bending and

stretching. The four most widely used methods to coat threads include- dip coating [2], sputtering [3], electro-less plating [4] and vacuum deposition.

Sputtering is the process where the metal particles are ejected when bombarded with a high-energy source and are deposited onto the thread. This process is able to achieve high uniformity of the metal film on the thread but is a fairly slow process. Electro-less plating deposits metals on the fabric using a combination of complex chemical reactions without the use of electricity. The process is able to provide uniform coatings around threads, but the fabrication process is fairly expensive. Vacuum deposition involves evaporation of metals using heat in a vacuum chamber. This requires specialized equipment not available in a typical textile manufacturing facility. The dip coating technique is when a thread is coated with a metal by immersion in a metal based solution. This process yields high conductivity of the thread but results in a non-uniform coating throughout the surface.

For all methods, the deposited metallic films are polycrystalline in nature and not as conductive as solid metal wires. Furthermore, the film thickness is around 1 μm . Metal films of this thickness tend to crack upon repeated bending and thus these threads degrade. These metal films are also not stretchable.

Regarding chemical vapour deposition (CVD), the substrate temperature needs to be high (between 300 - 1200 $^{\circ}\text{C}$) to initiate a reaction between the precursors needed to form a metal coating on the substrate. Typical fabrics like polyester, however, can only sustain temperatures up to 130 $^{\circ}\text{C}$ and thus metallic coatings cannot be formed on fabrics using CVD. CVD has, however, been used to coat fabrics with non-metallic but conductive coatings such as poly(3-alkylthiophene) nanoparticles [5] and the conductive polymer

polypyrrole [6]. Apart from these polymeric films not being as conductive as metallic films, CVD requires vacuum and specialized equipment, which is not typically available in standard textile plants.

Other coatings

Research is being done to design more bendable and stretchable conductive threads. These coatings are also easier to deposit using techniques like dip coating and drop casting. Materials being studied include conductive polymers like PEDOT-PSS [7], polyaniline and polypyrrole, carbon based materials like carbon nanotubes [8] [9] and graphene [10] [11] and nanomaterials including metallic nanoparticles [12] [13] and metallic nanowires [14] [15].

Polymeric coatings are flexible but have low conductivity, and suffer the problems of instability in the air due to absorption of moisture and oxygen [16] [17].

Metallic nanoparticle inks have been researched for several years for making continuous conductive films on different kinds of threads. Metallic nanoparticles can be printed and transferred onto fabrics using screen printing [18], brush coating [19] and spray coating [20]. Silver nanoparticles (AgNPs) are deposited on wool fibers using ultrasound [21], on silk threads to achieve antibacterials and colored conductive fibers [22] [23], impregnated cellulose fibers with AgNPs [24] and cotton fibers coated with gold and TiO₂ nanoparticle film to achieve self cleaning properties [25]. Despite the several advantages that the nanoparticles offer including ease of coating, high conductivity and plasmonic colors imparted to textiles, they pose certain problems. The report by Kim et al. [26] details

the few mechanisms how cracks can initiate, specifically for nanoparticle thin films. The stresses introduced in the thin film can be due to mismatched thermal coefficients of substrate and the metallic nanoparticle and due to the thermal energy during the annealing process. These stresses overall lead to micro-cracks being formed and delamination of the nanoparticle film. The work by Kim et al. [27] describes the use of silver nanowires along with silver nanoparticles to reduce the cracking of the silver nanoparticle thin film under mechanical stress.

Films of carbon nanotube (CNT) networks are alternatives to form conductive coatings on threads due to the low cost and high conductivity of individual CNTs. CNTs have been assembled to make yarns up to 30 cm in length by Fan et al.[28] which show high conductivity, strength and temperature resistance. CNT coated yarns have been produced using a chemical vapor deposition process by You et al. [29]. Despite the advantages, there are two major problem associated with CNT-based conductive threads. First, during the synthesis of CNTs, a mix of both metal and semiconductor tubes are produced, and the semiconductor tubes are not as conductive as the metallic tubes. Secondly, the junction resistance of CNTs is extremely high, despite the high conductivity along the length of the tube. This puts a limit on the conductivity that a CNT network can have [8] [9].

Stretchable conductive threads

For certain e-textile applications involving clothing, sporting apparel, strain sensors, etc., elastic stretchability is desired. There are multiple avenues by which a thread can be made conductive and also have/retain stretchability. One way could be by coating a stretchable thread with a conductive stretchable polymer. Another way could be wrapping a conductive thread around a stretchable polymeric element (epoxy or silicone). Stretchable

conductive fibers have been produced using chemical vapor deposited graphene by Hu et al. [30]. Work done by Zhou et al. [31] shows how to make a conductive stretchable cotton thread by coating CNT-cotton thread onto a silicone fiber to generate a conductive thread. Some commercially available solutions for stretchable conductive threads are supplied by Bekaert Fibre technologies, Dupont, Eeonyx Corporation, Textronics, Statex Shieldex (Germany), Baumlin and Ernst (Switzerland) and 3M. The existing conductive thread options have resistances in $k\Omega/cm$ range and also show a massive increase in resistance with few stretch cycles (a more elaborate description is in Chapter 4)

1.2.3 Conductive fabric

Conductive thread needs to be woven into fabric, either during textile processing or during post processing steps. Not only is this require extra steps, it can be difficult since conductive threads can be stiff or brittle, making them difficult to weave.

An alternative to weaving conductive threads into a fabric is to treat the fabric as a whole with a conductive material. Commercially available conductive fabrics have used various combinations of metals (silver, stainless steel, copper, nickel, cobalt, zinc and carbon) with fabrics (cotton, polyester, nylon and bamboo). These fabrics have conductivity in the range of $0.03 - 2 \Omega/\square$. These fabrics also provide EMI shielding from 6 - 80 dB [32]. These commercial textiles can be fabricated using textile metallization processes. Textile metallization is defined as depositing metallic particles on the surface of textiles using specialized techniques. These techniques primarily involve vacuum deposition, ion plating, electroplating and electro-less plating. Ion plating is a process that deposits the metal coating on the fabric by bombardment of ionized metal particles [33]. Electroplating is a

chemical process that coats the surface of the fabric using electric current [33]. The fabric is attached to the cathode and the metal to be deposited is the anode. The other methods are explained in Section 1.2.2. Each of these processes requires an elaborate fabrication setup, expensive machinery, adhesion problems, and the overall coatings are thick, brittle and non-uniform. Printing metallic inks on fabrics is another process used to coat fabrics. These inks are generally made of silver micro particles or nanoparticles. They are printed most commonly with using screen-printing, but other methods such as inkjet printing [34] can also be used. Most of these metallic inks have high viscosity and therefore, the coating is thick. The coating is thus stiff and non-breathable. Furthermore, the colour of the fabric becomes the colour of the inks, typically either black, grey, or copper colour which limits textile design.

Due to the drawbacks realized in the existing techniques available, new processes and inks need to be realized to coat fabrics to achieve conductivity.

1.3 Silver nanowire networks and existing work

1.3.1 Nanowires

A nanowire is a 1-dimensional cylindrical nanostructure which has a diameter less than 100 nm and a length up to 200 μm . Nanowires can be made from a wide variety of materials including metals, semiconductors and insulators and can be synthesized by a variety of top-down and bottom-up methods. One attractive property of nanowires is that simple and cost-effective methods exist to synthesize crystalline materials without the need for a single-crystalline lattice-matched substrate. Furthermore, these crystalline nanowires can

then be easily transferred, using solution deposition processes, onto a variety of substrates such as plastics and fabrics, and the nanowires are mechanically flexible unlike many thin-films and bulk materials.

1.3.2 Nanowire networks

A nanowire film is when nanowires are deposited as relatively flat layer on a solid substrate. A nanowire film is shown in Figure 1.1.

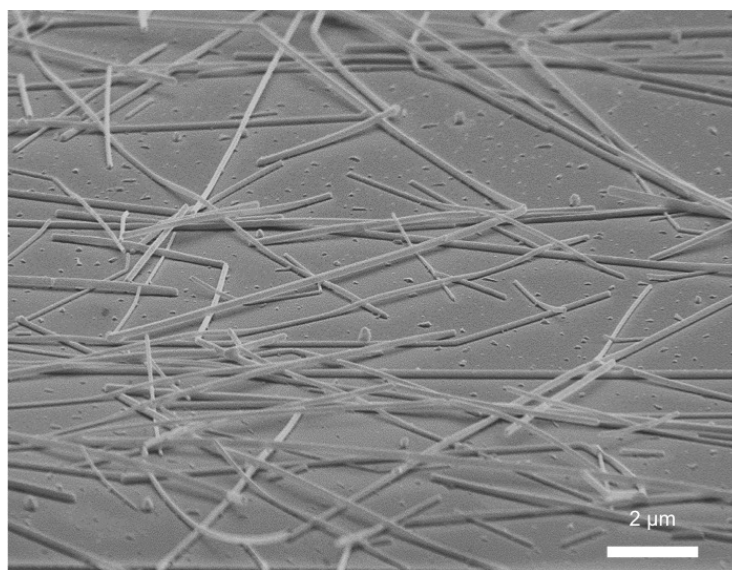


Figure 1.1: Nanowire film on the surface of a plastic substrate

The nanowires in the films are usually randomly oriented in the plane of the film. If the nanowires are semiconducting or metallic and the density of the nanowires is high enough, a network (also known as the percolation network) is able to conduct electricity from one end to the other of the film due to the junctions formed between overlapping nanowires.

If the nanowires are metallic, these junctions can be fused using heat via annealing. This greatly lowers the resistance, and is an advantage of using metallic nanowires over carbon nanotubes, which cannot be sintered. Because of the high aspect ratio of nanowires compared to nanoparticles, this conductive network can be achieved without fully covering the surface. There are many advantages of this being a mesh-like film rather than a continuous film:

1. The spaces between the nanowires can be larger than the wavelength of light and thus these films can be transparent [35].
2. They can relieve strain more easily than a continuous film, resulting in them being mechanically flexible [35].
3. They can use less material than a continuous film, which makes the film lighter in weight and potentially cheaper in material costs.
4. As will be shown in this thesis (Chapter 2), the spaces between the nanowires allow for the technique of transfer printing to be used, a technique which cannot be used to print continuous metal films.

Silver nanowire advantages and applications

Silver is the choice of metal used for nanowires for the purpose of the research due its exceptional conductivity, it is relatively stable in air (especially compared to copper and aluminum) and it has low toxicity [36]. Silver nanowire films can be conductive as well as transparent. Silver nanowire films are used as the transparent electrode [35] in commercial touch-screens like LGs 23" touch panel because they are lower in cost than the conventional materials typically used as transparent electrodes (conductive oxides such as indium tin oxide) as well have the potential of being mechanically flexible. The fact that silver nanowires are being used in commercial devices demonstrates that they are a commercially

viable technology.

Several techniques can be used to synthesize silver nanowires, but the most popular and convenient method is the polyol-synthesis process. The polyol process involves reduction of silver nitrate in solution using ethylene glycol in the presence of poly(vinyl pyrrolidone) (PVP). The nanowires grow along the [111] direction from seed nanoparticles (usually platinum), since the PVP passivates the {100} planes of the silver resulting in uniaxial growth. Each nanowire cross-section is pentagonal in shape, with 5 {100} faceted sidewalls [37].

1.3.3 Existing literature on silver nanowire coated textiles

There exist a few preliminary research studies that coat fabrics with silver nanowires using techniques like dip coating and brush coating. The research by Cui et al.[38] dip-coats cotton fabrics with silver nanowires for applications in heating of fabrics. The work done by Khalilabad et al. [39] shows the applications of silver nanowire coated-cotton for self cleaning and conductive textiles. Another paper by Cui et al.[40] shows the use of conductive AgNW- CNT networks for water filtration. Lastly, Madaria et al. [41] used spray coating to deposit AgNWs on fabric to achieve conductivity.

There are several similarities in the studies mentioned above. Firstly, all the fabrics that are tested are natural and hydrophilic fabrics, like cotton. Silver nanowires are hydrophilic due to the presence of the PVP polymer on them. Therefore, it is easier to coat natural fabrics with the nanowires compared to synthetic fabrics. Coating synthetic fabrics like polyester with dyes or nanomaterials is known to be problematic, due to pre-treatment

required for the textile before any deposition can happen [42] [43] [44] [45]. However, developing these processes for polyester is important since it is the most widely used textile in the world. Secondly, all the experiments are done using a high concentration of nanowires to make the natural fabrics conductive. The final conductive fabric is thus unable to retain its original color. Thirdly, the deposition methods used resulted in non-uniform density of nanowires on the fabric. Fourthly, as will be shown in this thesis, the large number of nanowires used is not cost-effective. Lastly, the solvents used in the existing techniques consist of organic, flammable liquids like ethanol and isopropyl alcohol (*IPA*), which are incompatible with the textile industry practices as they are a flammability hazard.

1.3.4 Units for resistance

For conductive fabrics and threads the most standard units to express resistance are Ω/\square and Ω/cm , respectively. Linear resistance is defined as

$$R_L = R/L \tag{1.1}$$

In case of a coating on a thread and a solid wire, the linear resistance of the thread is obtained by dividing the measured resistance across the two ends of the sample by the length between the two ends of the sample. For the thread, if the unit of seimens (S) is used, one would need to know the thickness of the coating present on the thread. Also using Ω/cm rather than S allows one to be better compare threads made using a conductive surface coating to those where the entire thread is conductive. And, using Ω/cm allows comparing threads of different diameters and lengths to one another.

For conductive fabrics, sheet resistance is defined as:

$$R_s = R * (W/L) \tag{1.2}$$

where R is the resistivity of the sample, R_s is the sheet resistance and W and L are the width and length of the conductive layer, respectively.

Sheet resistivity is defined as

$$R = R_s * t \tag{1.3}$$

The final units for sheet resistivity are Ω -cm.

For fabrics, sheet resistance rather than resistivity is used so that conductive coatings that are only on the top surface of the fabric can be compared to conductive treatments that extend throughout the thickness of a fabric. Furthermore, in this work nanowire networks do not form a continuous film and its thickness it difficult to define.

1.4 Organization of thesis

My research proposes adsorbing silver nanowires into fabrics like a color dye thereby making the fabric conductive. Not only natural but synthetic fabrics such as polyester are coated. Techniques and materials that are industrially compatible are chosen, and cost-effectiveness is considered as an important parameter. Chapter 2 describes how conductive fabric is

produced using several different deposition methods before the transfer-printing technique is settled on and optimized. It also details several characterization tests that are done to optimize the transfer printing technique and eventually the conductive fabric. Chapter 3 details the applications where these conductive textiles can be used. Chapter 4 discusses the methods used to fabricate a stretchable conductive thread using silver nanowire ink. Finally, Chapter 5 summarizes and provides prospectives on the work, as well as lists potential future work.

Chapter 2

Nanowire coating techniques onto fabrics

2.1 Motivation for silver nanowire conductive coatings

Fabrics can be made conductive using several different processes as outlined and described in Chapter 1. Considering the drawbacks of the various techniques in use, new processes need to be developed to build conductive fabrics. Not only the process, but the ink used to coat the fabrics needs to be refined as well to make the final product more flexible and stretchable. Metal plating and even printing a conductive ink (microparticle or nanoparticle based inks mostly) are common techniques but they can lead to high degradation rates after multiple bending cycles. The inks used to coat the fabric are typically silver, aluminum or copper. Silver is chosen for the work here because it is the most conductive of all metals, has good stability in air (particularly compared to copper) and is non-toxic.

Nanowires (NWs) are chosen over nanoparticles because their large aspect ratio allows a conductive film to be obtained with a mesh that doesn't fully cover the surface. This allows for less metal to be used, and the open mesh is much more flexible and bendable than a continuous film [46]. Furthermore, because the open spaces between AgNWs can be larger than the wavelength of visible light, it is possible for the films to be transparent, [46] allowing one to seamlessly impart conductivity into a fabric. Lastly, and as will become more clear by the end of this chapter, the open spaces between the NW network allows for a standard transfer printing process to work. This is because the adhesive can permeate between the NWs and trap the nanowire film on top of the fabric. A continuous film of nanoparticle ink, on the other hand, cannot be transfer printed since the adhesive cannot make contact with the fabric.

This chapter details the techniques that are used to coat silver nanowires (AgNWs) on fabric, the different critical parameters needed to optimize each process, cost estimates for each process as well as the advantages and disadvantages associated with each process. The chapter ultimately discusses the merits of transfer printing AgNW films onto fabrics. The motivation that drives the design of this new process is so that metallic NWs can be seamlessly integrated into the fabric like color dyes that have been used for several decades, and impart conductivity while still being flexible, bendable, washable and not mask the color or pattern of the fabric.

2.2 Experiments

Several techniques are experimented with to coat the fabrics with AgNWs. The four techniques used to coat fabrics in this work are:

1. Drop casting
2. Dip coating
3. Brush coating
4. Transfer printing

The primary objective of trying each technique is to reduce the resistance of the conductive sample using the least amount of AgNWs and therefore the least material cost. We only focused on techniques that are industrially compatible (i.e. use equipment and processes available in a typical textile manufacturing facility). For each of the coating methods, several parameters need to be optimized to obtain repeatable results. These conditions include annealing temperature and time, number of coats of AgNWs per sample, concentration of AgNWs, and the type of fabric to be used. Some parameters are added depending on the technique used for coating and will be discussed in the subsequent sections.

2.3 Drop casting

Drop casting works on the principle of the dispersion of the liquid along the surface of the substrate by shear forces. Drop casting samples are prepared by pipetting AgNW solution onto 100% polyester fabric supplied by MW Canada (Cambridge, Ontario). Drop casting is not discussed in detail here because the technique failed right away to produce any results on fabrics, due to heavy leaking of solvent through the fabric gaps, thereby leaving a thick layer of AgNWs in the one spot where they are pipetted onto the sample. This also resulted in the use of a very high amount of AgNWs to coat the entire fabric, thereby increasing both weight and cost of the final product.

2.4 Dip coating

Dip coating is a process that involves dipping the substrate into a solution to coat it with the desired dye or material. The dip coating process is shown in Figure 2.1. This is one of the easiest processes to perform in terms of coating the fabric with AgNWs. As such, dip coating was the method used in all the research papers in the literature where AgNWs were used to make a fabric or thread conductive [38] [39] [47] [48].

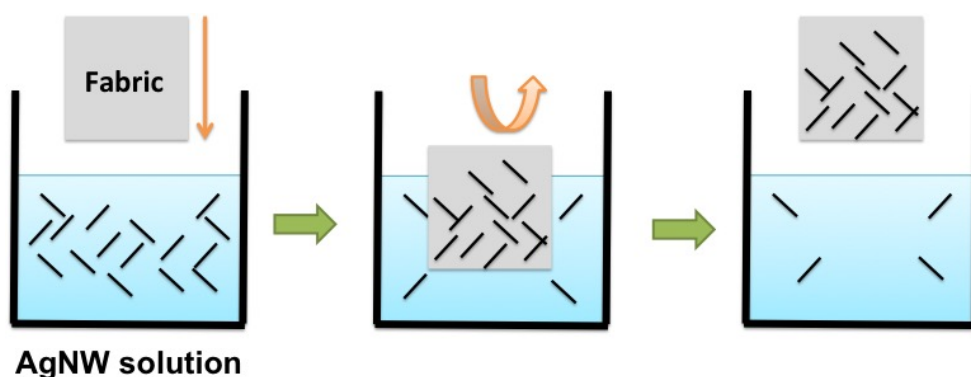


Figure 2.1: Dip coating fabrics with nanowires

2.4.1 Methods

A non-woven 100% polyester fabric, supplied by the company MW Canada, is coated with AgNW solution. The AgNWs were obtained from ACS Materials (Medford, Massachusetts, USA). The NWs have 40 nm diameters and 20 - 30 μm lengths and 50 nm diameters and 100 - 200 μm lengths and are dispersed in water. 3 x 3 cm pieces of fabric are coated with 1, 2 or 3 coats and then annealed in an oven at 130 °C for 1 hour in vacuum. The annealing step is required to sinter the overlapping NW junctions and greatly lowers the resistance of the NW network. The temperature of 130 °C is selected for two reasons. First,

the temperature corresponds to the temperature tolerance of the polyester fabric, beyond which the fabric starts degrading. Secondly, this temperature is a standard for heating and drying processes in the textile industry, which makes the whole technique more industrially suitable. The reason why the solvent for AgNWs is chosen to be water is because the textile industry avoids using flammable solvents for their processes to avoid fire hazards. As such, using water based inks or dyes is preferred over organic solvent based solutions.

The parameters optimized to achieve the best coating possible included AgNW dimensions, concentration of AgNWs, annealing temperature and time. The different condition combinations that are tried are shown in Table 2.1.

Table 2.1: Dip coating experimental parameters

AgNW diameter (nm)	AgNW length (μm)	AgNW concentration (mg/mL)	Annealing temperature ($^{\circ}\text{C}$)	Annealing time (mins)
40	30	20	100	45
40	30	10	110	60
40	30	4	120	60
40	30	3.33	130	75
40	30	2.5	130	75
50	200	0.5	130	60
50	200	2.5	130	60
50	200	5	130	60
50	200	10	130	60

In initial experiments, the AgNWs did not adhere well to the polyester fabric and a conductive network could not be obtained. This is because the polyester fabric is hydrophobic and the AgNWs, due to the PVP polymer coating, are hydrophilic. Because of this difference, the AgNWs do not adhere well to the synthetic, polyester fabric. Thus, a

few surface modification techniques are tried to increase the wettability and hydrophilicity of the polyester fabric. The chemical dip-based modifications included dipping in sodium hydroxide (NaOH), acetic acid (AA), and F-127 surfactant with and without cellulose. The next few sections explain the different modification techniques, why some worked and why others did not.

Sodium hydroxide surface modification

Sodium hydroxide modification is a standard and commonly used technique in industry to scour fabrics and to improve the hydrophilicity of polyester fabric. The NaOH treatment has a threefold advantage for the fabric samples. First, it helps clean off the impurities that are present on the fabric surface. Second, it helps increase adhesion of AgNWs to the fabric by making the polyester more hydrophilic. Lastly, NaOH helps with the liquid retention capacity of the fabric. NaOH helps hydrolyze the surface of polyester by forming hydrophilic bonds on the polyester chains. This is done by introducing polar groups on the surface of polyester thereby increasing the bonding of the polyester with water molecules [49]. The polyester fabric is dipped in varying concentrations of NaOH for 6 mins. The NaOH dipping is tried both at room temperature and at a temperature of 75 °C. The wet NaOH modified fabric is then coated with AgNWs without removing the excess NaOH solution. The different concentrations of NaOH used are 6.25 mM, 50 mM and 500 mM.

Although the SEM images (Figure 2.2) show a very small difference in the density of NWs that stick to the threads, the overall resistance numbers in Table 2.2 show that the modification with heated NaOH gives better resistance numbers compared to room temperature NaOH modification. Also, during the scouring of polyester fabrics when the synthetic dyes are applied, heated NaOH is used in industry as well to improve the adhe-

sion of dyes to the fabric [49].

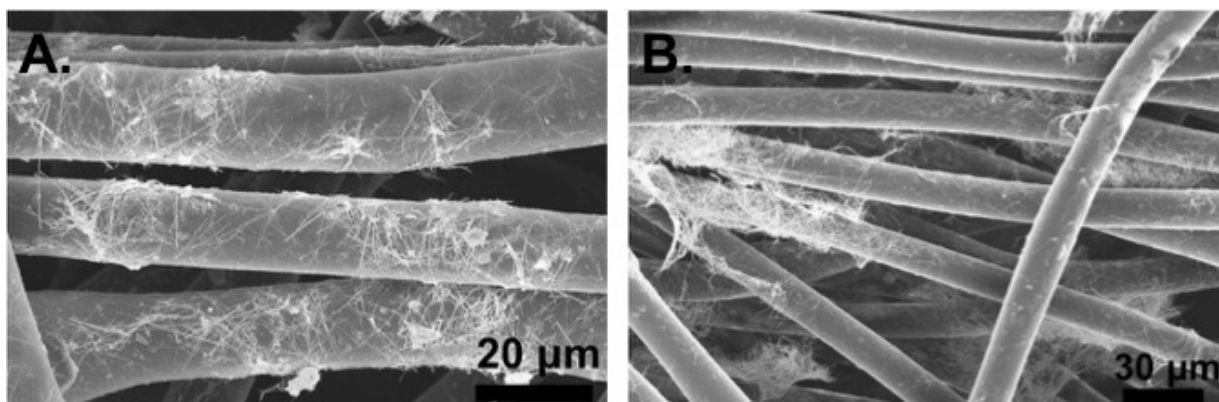


Figure 2.2: SEM images of AgNW adhesion A. Room temperature NaOH modification B. Heated NaOH modification

For NaOH treatment of threads for concentrations of 6.25 mM, 50 mM and 500 mM, some damage is observed for the threads as the concentration of NaOH increases. This can be observed in the Figure 2.3. For the 50 mM sample in Figure 2.3B can be seen that the surface of some polyester filaments have a pitted surface and no nanowires sticking to it. As for the 500 mM sample in Figure 2.3C , the NaOH has completely broken some of the polyester filaments into pieces.

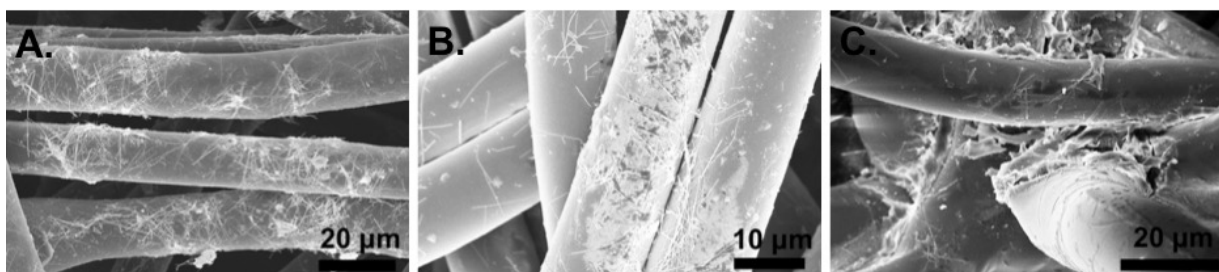


Figure 2.3: Damage to polyester threads with increasing concentrations of NaOH A. 6.25 mM B. 50 mM C. 500 mM

Therefore, since the 6.25 mM concentration still caused adequate adhesion between the polyester and the AgNWs, and 6.25 mM is a common NaOH concentration used in the textile industry, it was this concentration that was ultimately chosen in this work.

Acetic acid surface modification

The polyester fabric is dipped in varying concentrations of acetic acid for 30 mins and then the wet fabric is coated with AgNWs. The different concentrations of acetic acid used are 5 mM, 50 mM and 500 mM. The adhesion obtained with acetic acid surface modification was not as strong as was obtainable with NaOH and thus acetic acid was not chosen as the preferred medication method. For acetic acid, a similar trend is observed, as seen in the SEM images in Figure 2.4, where with increasing concentration of acetic acid, thread damage was observed. Also, NaOH is an industry standard for scouring fabrics and is therefore a regular chemical used in the textile industry.

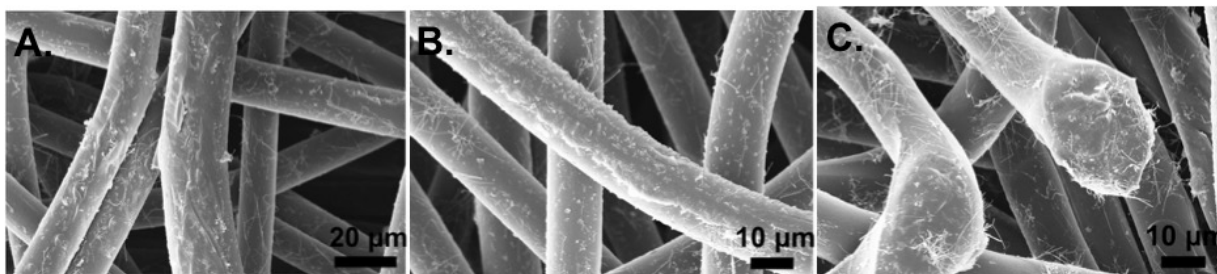


Figure 2.4: Damage to polyester threads with increasing concentrations of Acetic acid A. 6.25 mM B. 50 mM C. 500 mM

Pluronic F-127 surface modification

Pluronic F-127 is a known biological dispersant. It is a non-ionic surfactant polyol with a molecular weight of 12500 dalton. It has been discovered to also be an effective dispersant of AgNWs and helps them bind to Polyethylene terephthalate (PET) [50], which is a polyester-based plastic. It was found here that F-127 helped with reducing NW aggregates present in the AgNW solution. F-127 is used with and without cellulose to experiment with improving the adhesion of AgNWs to the hydrophobic polyester fabric. The cellulose is used to thicken up the solution, and since cellulose is hydrophilic, it may help with the adhesion of AgNWs onto the hydrophobic fabric. When F-127 is used for surface modification with or without cellulose, it was observed that it did not help with the adhesion of AgNWs to fabric as no NWs stuck to the fabric. Therefore, F-127 was not used for final surface modifications in this work.

2.4.2 Results and discussion

The 3 x 3cm samples of fabric were dipped in the AgNW solution in water for 1 min. Then the samples are retrieved from the AgNW vial and left in air to dry for 15 mins.

The modification time chosen when using heated NaOH has been previously experimented with and confirmed in the work by Yahya et al. [51]. During the industrial textile dyeing process, when acetic acid is used, the fabrics are heated in acetic acid. Both 30 mins and 60 mins time are tried, with 30 mins used to reduce the time for modification. The SEM images for the 30 mins dip shows silver nanowires sticking to the fabric and good resistance numbers, which is why the number is used. Compared to 60 mins of modification dipping time, 30 mins modification sample resistance numbers are similar. Therefore, less time modification is used.

Depending on the surface modification technique used for the polyester cotton fabric, the resistance of the AgNW coated fabric had variation. As seen in Table 2.2, the best results for conductivity are obtained for heated NaOH modification of the fabrics. The dip coating numbers are obtained for one coat in a 5 mg/mL solution of AgNWs.

Table 2.2: Dip coating sample resistance with different fabric modifications when coated with AgNWs

Modification type	Sample number	NW Concentration (mg/mL)	Dipping time in modification (mins)	Resistance (Ω/\square)
No modification	1	5	0	2.7
No modification	2	5	0	6.07
NaOH	1	5	6	2.2
NaOH	2	5	6	2.5
Heated NaOH	1	5	6	1.14
Heated NaOH	2	5	6	0.78
Acetic acid	1	5	30	3.45
Acetic acid	2	5	30	6.58

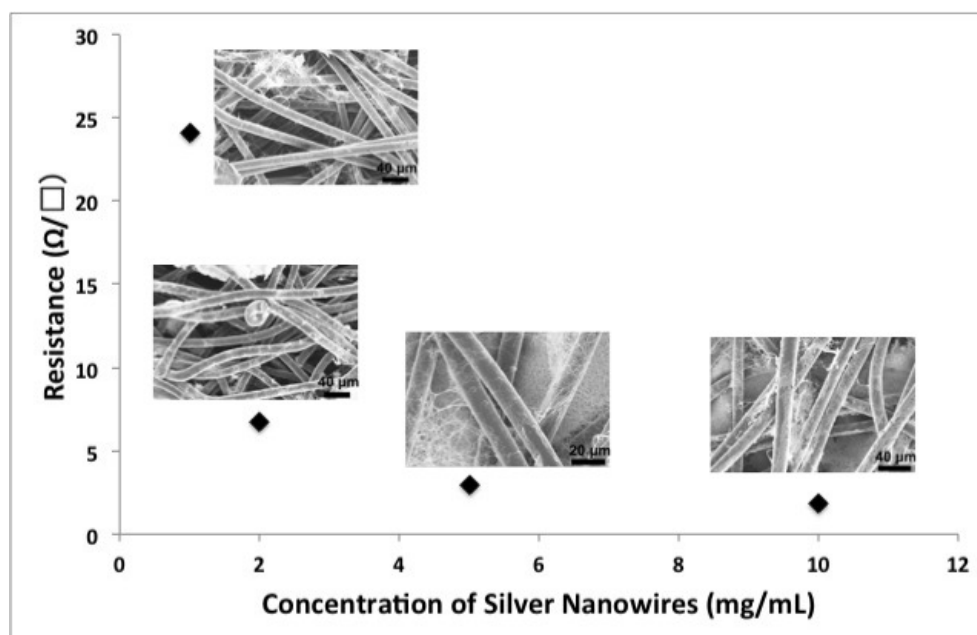


Figure 2.5: Dependence of the fabric resistance on the NW concentration in the dipping solution

As can be seen in the SEM images in Figure 2.5, as the concentration of AgNWs increases, the amount of AgNWs adsorbed onto the fabrics increases. A higher density of NWs means that there are more metallic pathways available for conduction, leading to a lower resistance, as is confirmed by the resistance numbers in the plot.. To investigate the quality of the coating, SEM image was obtained on the fabric before and after coating. The polyester fabric, without any coating, is shown in Figure 2.6. There are wide open spaces between threads. When the polyester fabric is dip coated with AgNWs, as is imaged in Figure 2.7, the NWs not only stick to the threads of the fabric, but also aggregate in the gaps present between the threads. The NWs in the spaces between threads was also observed in all other papers where AgNWs were used to modify fabric [38] [48].

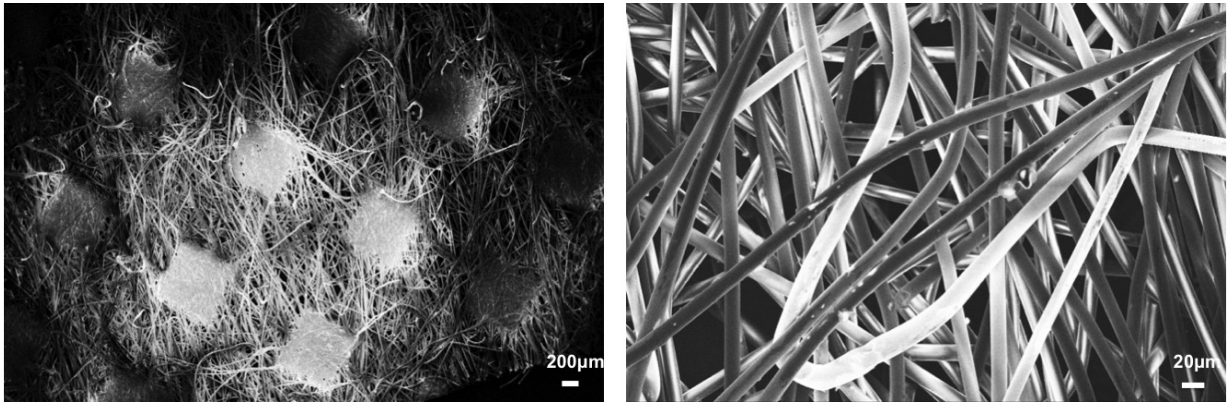


Figure 2.6: SEM image of as-received non-woven polyester fabric

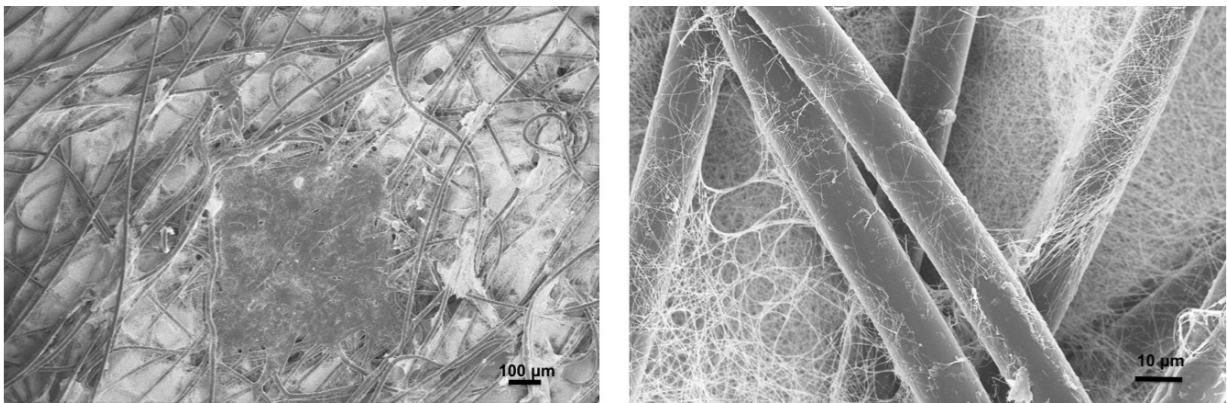


Figure 2.7: SEM image of non-woven polyester fabric dip-coated with AgNWs

There is poor uniformity of the AgNWs on the polyester fabric. For example, we can see in Figure 2.7 that some threads are coated with a higher density of NWs than others, and some spaces between threads have a denser network of NWs than others. Even with this non-uniformity, low sheet resistances such as those shown in Figure 2.5 are still obtained. This is because of the high density of NWs.

As mentioned above, the dip coating technique results in NWs not only coating the

individual threads, which in total have a very high surface area, they also coat the spaces between the threads. And the NWs are absorbed throughout the entire thickness of the fabric, which is 0.12 mm in this case. Thus, because the NWs are spread out over a large area and volume, a very high NW concentration in the fabric is needed to obtain a percolative network. When concentrations less than 0.5 mg/mL were used, the fabric was not conductive. The papers in the literature which dip-coat fabrics with AgNWs to obtain conductivity also use a very high NW [38] [39] [48]. The major problem with this is cost. Ag is an expensive metal, and AgNWs are even more expensive than bulk Ag, costing \$32/g in materials alone [52]. This drawback is not mentioned in the literature, but the cost is too high to be used commercially. Fabric samples were weighed before and after NW coating to estimate the mass of NWs that was added during coating. The added mass was multiplied by \$32/g and the results are shown in Table 2.3. It can be seen that the costs are exceptionally high. Although dip-coating is simple and results in high conductivity, the high cost of the NWs that need to be used makes this an unsuitable method to obtain conductive fabrics.

Table 2.3: Dip coating sample cost for AgNW coatings with different resistances

Concentration of AgNWs (mg/mL)	Weight of NWs in sample (mg/m ²)	Resistance (Ω/\square)	Cost (\$/m ²)
1	17.8	28.5	689
2	30.3	2	1200
5	36.4	1.2	1316
10	41.8	0.7	1617

Lifetime tests of the dip-coated fabrics were done. Two samples were dip-coated with AgNWs with a 5 mg/mL concentration. Their initial sheet resistance was 1.2 Ω/\square . One

sample was left in air for 18 months, while the other was kept in vacuum during that same time. After this time, the resistance of the sample left in air rose to $10.4 \Omega/\square$, and the one kept in vacuum remained at a resistance of $1.2 \Omega/\square$. Furthermore, Figure 2.8 shows the appearance of the two samples and the sample left in air is darker. The resistance and colour change is likely due to the oxidation of silver in the air. The dark grey of the coating is similar to what is seen when silver corrodes in air [53]. These tests indicate that AgNW dip-coated conductive fabrics need to be protected from the environment if they are to perform well over long periods. A passivation layer is likely required.

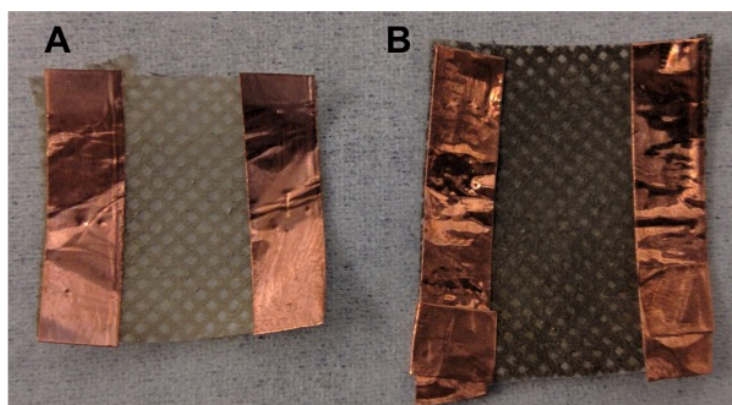


Figure 2.8: Dip coated samples with resistance starting at $1 \Omega/\square$. Sample A was preserved in vacuum and sample B was left in air for 18 months

2.5 Brush coating

Brush coating is a process similar to painting with a brush on a canvas. The process is shown in Figure 2.10. Brush coating is expected to be more of a surface-only coating compared to dip coating, which as discussed in the section above coats through the depth of the fabric. A rod coating method, such as Mayer rod coating, is a solution deposition

technique, which typically results in a uniform thickness of solution being deposited. It cannot be used for fabrics, however, because the solution seeps through the spaces in the fabric where the solution is initially deposited and the rod therefore cannot draw the solution across the surface. Thus, a brush-coating process was tried.

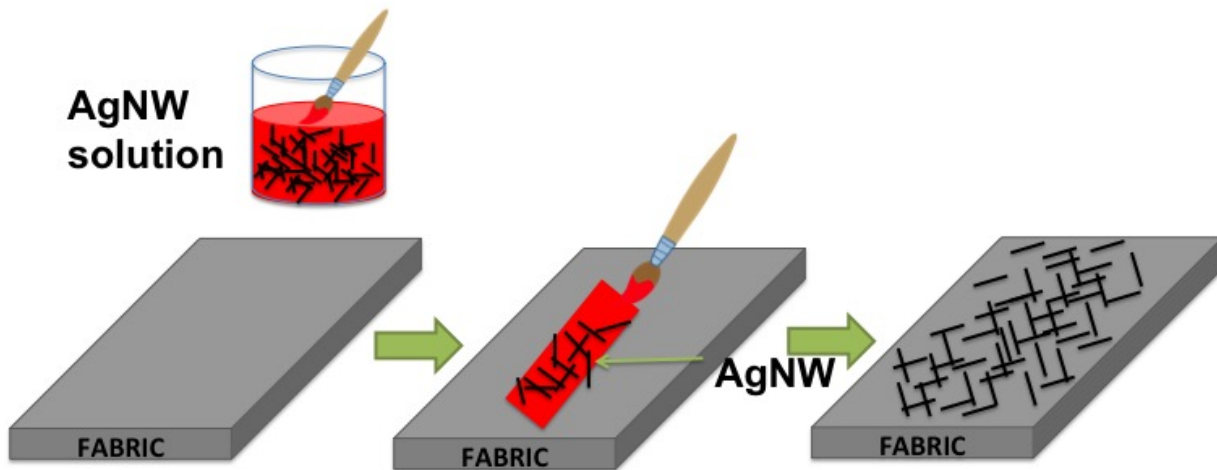


Figure 2.9: Brush coating silver nanowires on fabric

2.5.1 Methods

The AgNWs used are 40 nm in diameter and 10 μm in length, are dispersed in water, and are purchased from ACS materials (Medford, Massachusetts, USA). A simple paintbrush is used to coat the fabrics with AgNWs. Since the NWs are in water, direct application of the solution to the fabric caused the solution to seep through the fabric, due to the gaps present between the interwoven threads of the polyester fabric obtained from MW Canada (same as the one used in the dip coating technique). For this reason, a thicker solution needs to be used for coating purposes. Carboxymethyl cellulose (CMC) is used

as the thickener for the AgNW solution with a 1% by weight concentration. The different AgNW concentrations used for coating are 5, 2 and 1 mg/mL. Coatings are deposited after fabric pre-treatment with heated NaOH, CMC, pre-heating of the fabric, and without any pre-modification techniques. It is found that the best resistance numbers were obtained for heated NaOH pre-treatment (80 °C, 6 mins) before the coating process. 2 brush coats are done to coat the area of the fabric. On average, about 500 μ L of solution is used with every single brush coat, and the size of the fabric samples are 4 cm x 4 cm. Once the coating is completed, the fabric is annealed at 120 °C for 60 mins in vacuum.

2.5.2 Results and Discussion

Figure 2.10 shows the resistance of AgNW films brush-coated on polyester fabric with different NW concentrations. The resistance numbers obtained are higher for brush coating compared to dip coated samples. SEM analysis was done to determine why.

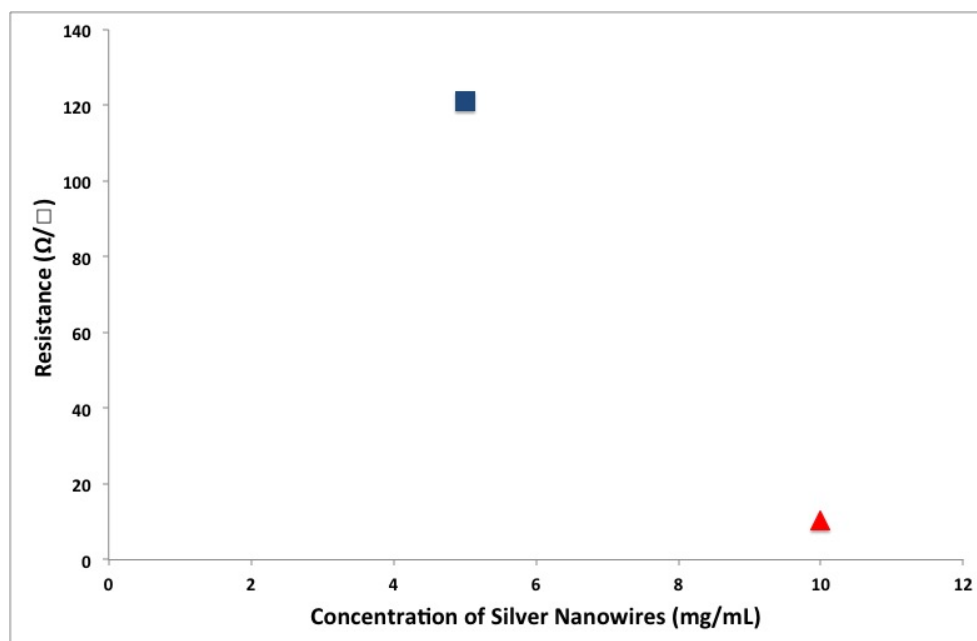


Figure 2.10: Sheet resistance of polyester coated with AgNWs using the brush coating technique, for two different NW solution concentrations

As seen in the SEM image in Figure 2.11, at 5 mg/mL AgNW solution concentrations, the brush coating results in a very non-uniform deposition of NWs. The surface of some threads are coated more than others. As for the spaces between threads, some are filled with NW clumps while others are not. This technique still causes seeping of AgNWs through the fabric resulting in them being distributed throughout the thread layers. Thus, the nanowires don't connect into a percolative network well. Due to the non-uniformity of the coating, and the resistance is quite high for each of these samples.

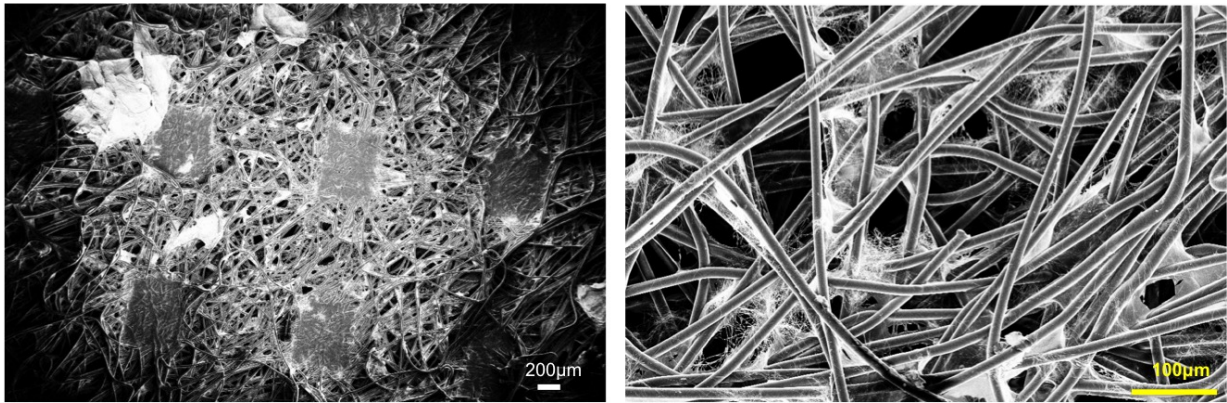


Figure 2.11: SEM image of non-woven polyester fabric coated with AgNWs using brush coating

The mass of AgNWs used per area was not measured, as the SEM images and resistance results make it clear that brush coating is not a good technique for depositing AgNW coatings. The NWs are deposited very non-uniformly and thus a high number of NWs are required for percolation. Therefore, like dip-coating, the cost of NWs to make a conductive fabric is prohibitively high. To be able to use less NWs, they should instead only be deposited on the top surface of the fabric and thus transfer printing was investigated.

2.6 Transfer printing

2.6.1 Introduction to transfer printing

Transfer printing is a technique used to transfer designs printed on transfer paper or plastic onto another substrate by application of heat and pressure. Transfer printing is a common process in use since the 1750's. Some of the first transfer prints were done on ceramics. One of the first patents that describes the process of transfer printing dyes on polyester fabric

was filed in 1966 [54]. The patent by Mizutani et al. (1972) [55] outlines the process of colored heat transfer printing on polyester fabric. Transfer printing is a common technique used in the textile industry. The fabrics printed using this technique range from natural fabrics like cotton and silk to synthetic fabrics and blends like polyester, rayon and nylon.

Transfer printing has been used to transfer AgNW networks onto polyethylene terephthalate (PET) [56]. However, there have been no studies done that use transfer printing for transferring NW films onto fabric. It was tested here not only because it is a simple and industrially compatible technique, but it results in NWs being deposited on the surface of the fabric only, rather than spread out throughout the textile like with dip-coating and brush-coating methods. Depositing nanowires on the surface only allows for a percolative network to be obtained with much less NWs, and therefore is much more cost effective.

2.6.2 Transfer paper basics

Transfer paper is an essential element in the transfer printing process.



Figure 2.12: Schematic of light transfer paper

Transfer paper, as shown in Figure 2.12, consists of printing paper coated with a polymer film. In the experiments here, the polymer film is ethylene vinyl acetate (EVA). The EVA on the transfer paper acts as an adhesive, which helps with two steps of the printing

process. One, it holds the AgNW ink pattern in place on the paper before transfer. Two, when the pattern is transferred onto the fabric using heat and pressure, it also adheres to the fabric thereby acting as a binder between the ink and the fabric. When heat and pressure are applied to the transfer paper during the transfer process, the EVA is released from the paper backing and transfers onto the fabric. The pressure application helps with pressing the ink pattern into the polymer substrate, which then is released onto the fabric when heat is applied. The heat helps with the release mechanism of the EVA polymer from the transfer paper to the fabric.

The above describes what is called light transfer paper, which is predominantly what is used in this project and is the more typical transfer paper. When the NWs are transferred, they end up in direct contact with the fabric with the polymer coating on the top. There exists another type of transfer paper called dark transfer paper. This transfer paper has a different architecture compared to light transfer paper. The dark transfer paper is shown in Figure 2.13.

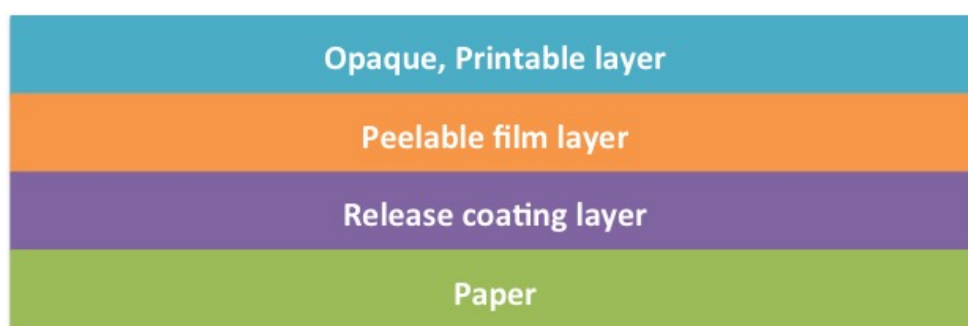


Figure 2.13: Schematic of dark transfer paper

As shown in Figure 2.13, the dark transfer paper consists of four layers. The bottom

layer is the paper. On top of the paper is a release layer polymer, which basically attaches the layer third from the bottom (aka the peelable layer) to the paper. The top layer of this transfer paper consists of multiple crosslinking polymers that can enable a variety of features- opacity and printing inkjet or laserjet inks.

The top paper, on which the AgNW ink is printed. It consists of a polymeric binder (could be acrylic or polyurethane in this case) and a crosslinking agent (could be epoxy, carbodiimide or oxazoline polymer - the actual composition is unknown from the vendor and is proprietary), which helps the NWs to stick to the dark transfer paper [57]. The orange layer, which is the peelable layer, consists of an adhesive backing. This layer melts to penetrate into the fabric, thereby attaching the NW film to the fabric when heat and pressure is applied.

After the NWs are deposited on the surface of the crosslinking polymer, the polymer is peeled away from the backing paper (by hand in this work) and the backside of the polymer film is then stuck onto the fabric (again, by hand in this work). The result is that the NWs are not in direct contact with the fabric, but rather polymer exists between the NWs and the fabric. The NWs remain on the top surface. This allows for easier electrical access to the NWs, which is useful in some applications.

Throughout this chapter, when not specified it is light transfer paper being used.

2.6.3 Experimental methods

Transfer printing technique is a multi-step printing process (Figure 2.14).

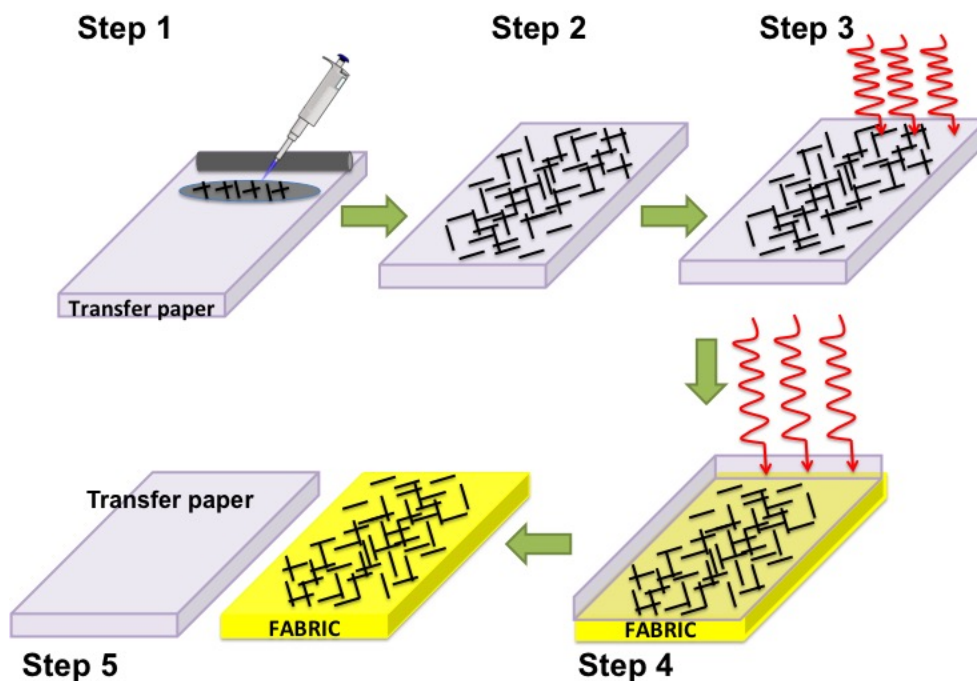


Figure 2.14: Transfer printing films of silver nanowires onto the surface of fabrics

Several parameters were optimized to determine the best conditions for transferring AgNWs onto fabric. These parameters include type of transfer paper, numbers of coats of NWs, annealing temperature, heat press pressure, transfer temperature and peel off speeds of the backing paper. The Table 2.4 below shows the different parameters that are experimented with to optimize the process.

The different parameters for the process and how they are optimized are explained in

Table 2.4: Parameters for transfer printing

Transfer paper	Number of coats	Annealing temperature	Heat press pressure	Heat press temperature	Post deposition techniques
Light transfer paper (inkjet or laser jet)	2-4	90-150 °C	Low, Medium and High	163-213 °C	Roller Pressing DC current

detail in the subsequent sections.

Deposition of NW films on transfer paper

First, the AgNWs are coated on transfer paper using a Mayer rod. The AgNWs are obtained from ACS Materials (Medford, Massachusetts, USA). The AgNWs used to coat the transfer paper have a diameter of 40 nm and lengths of 200 μm and are dispersed in ethanol. The different concentrations of AgNWs which were coated on the transfer paper were 2.5, 5, 7.5, 10, 15 and 20 mg/mL.

The Mayer rod assists in controlling the thickness of the deposited AgNW film and therefore results in good uniformity of NWs across the area of the transfer paper. The Mayer rod used is RDS 20, which gives a 50.8 μm wet film thickness. The AgNW coating varied anywhere from 1 to 5 coats per sample depending on the concentration of the NWs and thickness desired to obtain resistance under 100 Ω/\square . The transfer paper is commercially obtained from Joto Paper Ltd. (Coquitlam, British Columbia, Canada), Stahls Canada (Concord, Ontario, Canada) and Transfer Paper Canada (Mississauga, Ontario Canada). Several different transfer papers are used to figure out which would work best for transfer printing of AgNWs on fabrics. The list of the different transfer papers used

and the companies they are supplied by are listed in Table 2.5.

Table 2.5: Transfer paper experiments

Name	Company	Type	Roughness
CL120	Joto Ltd.	Laserjet	Low
CL135	Joto Ltd.	Laserjet	Medium
CL140	Joto Ltd.	Laserjet	Medium
Inkjet light	Joto Ltd.	Inkjet	High
Inkjet dark	Joto Ltd.	Inkjet	High
Inktra	Stahls	Laserjet	High
Jet Pro Soft stretch	Transfer paper Canada	Inkjet	High

As stated before, Mayer rod coating is used to coat the transfer paper with AgNWs. Figure 2.15 shows how Mayer rod coating works.

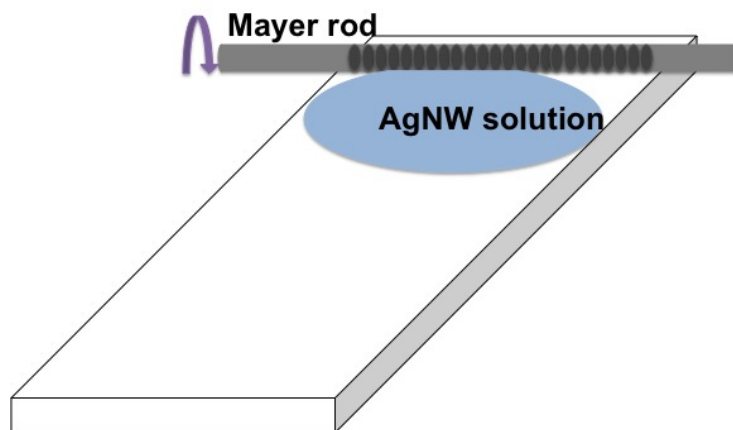


Figure 2.15: The Mayer rod coating technique

200 μL per 8 cm width of AgNW solution in ethanol is pipetted in a line at one end of the transfer paper (dimensions of the transfer paper are 8 cm x 8 cm). The Mayer rod

is then used to coat the transfer paper with the solution by dragging down the liquid ink along the length of the transfer paper. The use of 200 μL of AgNWs and one drag-down with the mayer rod is counted as 1 coat. Samples with 4 coats, which gave the highest uniformity for AgNW coatings in terms of resistance numbers and had a total of 800 μL volume of AgNW solution.

AgNW solution was also mixed with cellulose to try to potentially increase the adhesion of AgNWs to the transfer paper and to improve the transfer onto the fabric. It was found that the cellulose did not help with the transfer, but rather increased the resistance of the NW coating on the transfer paper. Therefore, cellulose was no longer used for further experimental purposes.

For optimizing the annealing temperature of AgNW on the transfer paper, the different temperatures experimented with depended on the heat tolerance of the transfer paper. If the temperature is too high, the transfer paper deforms in the form of tiny bumps on the surface of the paper. This causes the NW film to be disturbed out-of-plane, reducing the number and quality of NW overlapping junctions and therefore an increased resistance of the sample. If the temperature is too low, the NW junctions do not fuse as well, thereby causing high resistance as well. The different temperatures tested were 90 $^{\circ}\text{C}$, 100 $^{\circ}\text{C}$, 120 $^{\circ}\text{C}$ and 150 $^{\circ}\text{C}$. The best annealing temperature is found to be at 120 $^{\circ}\text{C}$. The transfer paper is then annealed at 120 $^{\circ}\text{C}$ for 60 mins in a vacuum oven which helps sinter and thus lower the resistance between overlapping nanowires.

AgNWs due not completely fuse at 120 $^{\circ}\text{C}$. For AgNW networks on glass, for example, the optimal temperature to fuse the NWs and obtain the lowest resistance is 200 $^{\circ}\text{C}$

[58]. Since an annealing temperature above 120 °C could not be used due to the tolerance of the transfer paper, three additional processes implemented either before or after the anneal are experimented with to lower the junction resistances. The three methods are polyvinylpyrrolidone (PVP) removal using chemical treatment, roller pressing of the transfer paper and passing DC current through the annealed AgNW sample.

PVP removal

PVP remains on the surface of the AgNWs after their polyol synthesis [37]. However, PVP is not conductive and introduces resistance between overlapping NWs. This PVP can be removed with a high temperature anneal, but because annealing temperatures are limited due to the thermal budget of the transfer paper, PVP must be removed chemically. In this work, after the nanowires are deposited on the transfer paper, they are washed with water and ethanol before thermal annealing, which is a technique known to remove PVP [59].

Roller pressing

Roller pressing is employed to mechanically press the NWs into the transfer paper, which both reduces the surface roughness of the sample and ideally presses the overlapping NW junctions into one another. This would reduce the resistance of the sample. The hot rolling press (MSK-HRP-01, MTI Corporation, Richmond, USA) is shown in Figure 2.16.



Figure 2.16: Hot rolling press

The roller pressing was done at room temperature. The sample is rolled twice, both times along the length of the sample. The rollers are initially separated by 70 mm. The pressing distance is reduced progressively from 70 mm to 5 mm to figure out the ideal pressing distance. The resistance was tested after every press to see how the resistance of the sample changed. It is good to note that the roller pressing technique is roll-to-roll compatible, and so it would fit well into an industrial process.

DC current application for NW welding

DC current is passed through the NW network after annealing of the AgNW coating on transfer paper. The current creates Joule heating, particularly at the high resistance NW junctions, and can help lower the resistance. Currents of 0.1 -1 A are tried for a sample

size of 4 cm x 4 cm.

Transfer process

Once the NWs on transfer paper are annealed in the oven to fuse the NWs, it is placed design down on the fabric of choice and pressed using a heat press. Prior to this, the fabric is cleaned by submersion in a solution of liquid cloth washing detergent and water for 15 mins. The solution is stirred with a stir bar while heated with a hot plate at a temperature of 40 °C. Copper tape is attached to either end of the fabric prior to the transfer of the AgNW network so that the NWs could be electrically accessed after transfer. Since the EVA polymer coats the top of the AgNWs, the copper tape cannot be placed after NW transfer. The AgNW film is then transferred onto the fabric with a heat press purchased from FlexHeat (Brampton, Ontario, Canada), which is an 11" by 15" digital heat press. The sample is then retrieved from the heat press and the paper is peeled off by hand, leaving the AgNW film stuck to the fabric. The polymer coating is not removed from the sample as it provides sample protection from air and NWs from falling off the fabric. The final fabric sample looks like Figure 2.17.

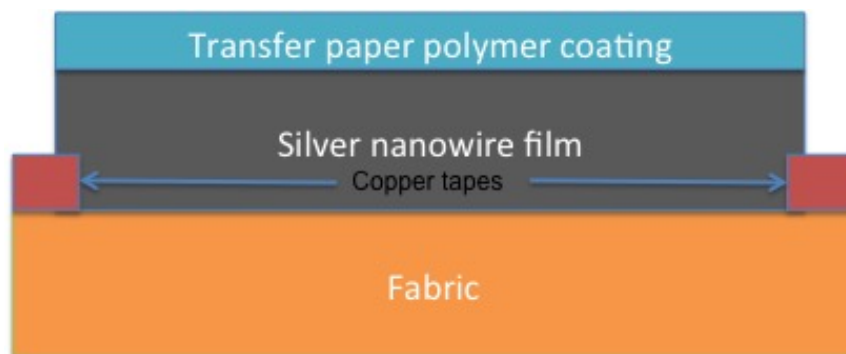


Figure 2.17: Schematic of the transfer printed fabric sample

The major parameters that needed to be optimized for the heat press included- heat press temperature and pressure, transfer time, type of transfer paper used and peel off time. The temperatures tested during the heat press step are 163 °C, 177 °C, 190 °C, 204 °C and 218 °C. For transfer time, times of 20, 30, 45, 60, 75, and 90 s were tried. For pressure, low, medium and high pressure settings of the heat press were tried. Peel off time is defined as the time between retrieving the sample from the heat press after the pressing and starting the peel off of transfer paper from the fabric. Peel off times between 10 s- 60 s were tried.

Several different fabric samples were tested to optimize the transfer printing technique. All the fabric samples were purchased from Fabricland. The list is shown in Table 2.6.

Table 2.6: Fabric contents

Name	Composition
Regular cotton	100% cotton
Interfacing cotton	100% cotton
Cotton silk blend	70% cotton and 30% silk
Viscose linen blend	70% cotton and 30% silk
Viscose linen blend	70 % viscose and 30% linen
Regular rayon	100% rayon
Polyester cotton blend	65% polyester and 35% cotton
Interfacing polyester rayon blend	90% polyester and 10% rayon
Interfacing polyester rayon blend	60% polyester and 40% rayon
Regular polyester	100% polyester

Parameters for the different transfer papers listed in Table 2.5 that are compared, beyond measuring the resistance of the sample once AgNW coating is applied, are:

1. Roughness of the polymer (EVA) on the paper
2. Polymer packing style on the paper

3. NW density that gets deposited on the paper
4. Heat tolerance of the paper

Characterization

Scanning electron microscopy (SEM) is used to image the AgNW films on various substrates, the bare transfer papers, and the bare fabrics. SEM analysis gives information about the density and distribution of the AgNW film across the transfer paper and also an understanding of the fabric structure. It is also used to understand the transfer paper characteristics like roughness and polymer distribution on the paper.

The sheet resistance of the samples is measured using a multimeter applied across the two copper tapes. The sheet resistance is calculated in Ω/\square by measuring the resistance and the knowing the sample dimensions (width and length). The formula for calculating the sheet resistance is:

$$\textit{Sheet resistance} = R * (W/L) \tag{2.1}$$

The characterization tests used to quantify the results of the transfer printed AgNW fabric are listed in the Table 2.7, along with the purpose and equipment used to perform the testing.

Table 2.7: Characterization tests for transfer printed fabrics

Test	Purpose	Equipment used
Electrical Characterization	To measure the sample resistance	Multimeter
Mechanical test	To measure the change in the sample resistance with extended and multiple bending and folding cycles, separately	Multimeter, A 120 mm radius rod for bending consistency
Lifetime testing	To measure the change in sample resistance over time (30 days)	Multimeter
Washing tests	To measure the change in resistance with variable washing techniques	Multimeter, Laundry detergent, Hot plate and Stir bar
Cost calculation	To compute the costs associated with transfer printing of AgNWs on fabric	SEM, ImageJ

Cost Calculations

For cost calculations, the transfer paper is coated with AgNWs and without the annealing step, analyzed under the SEM. Image J software is then used which counts the black and white pixels of the image to quantify the surface coverage of the AgNWs. The surface coverage is then converted into the volume of the NWs by knowing the cross-sectional shape and size of the NWs, which then can be converted into mass per m^2 by using the density of silver. This mass in g/m^2 is then multiplied with the cost of growing NWs at \$ 32/g to get the cost of NWs in $\$/\text{m}^2$ [52].

The cost could only be estimated for lower densities of NWs coated on the transfer paper since at higher densities there is too much NW overlapping. Three data points

at 2.5, 5 and 7.5 mg/mL concentration of AgNWs were used to generate an equation to estimate costs at higher NW concentrations.

2.6.4 Results and Discussion

NW films on transfer paper

Figure 2.18 is an SEM image of a NW network on transfer paper. The NW density is quite uniform, except for localized areas seen in the left of the figure. These regions are because the transfer paper is not flat, and out-of-plane bumps in the EVA are not well coated with NWs. Once the AgNW network is transferred on the fabric, it cannot be imaged with a SEM because of the ethylene vinyl acetate present on top of the AgNW network.

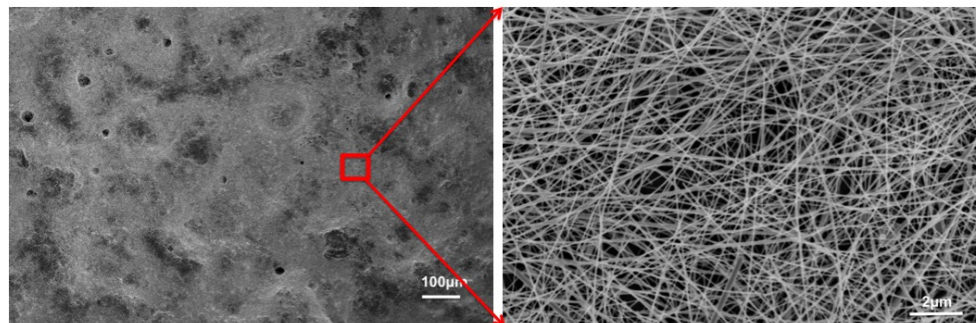


Figure 2.18: NW network on transfer paper (before transfer onto fabric)

PVP removal helps lower the resistance of the transfer paper samples. As can be seen in Figure 2.19, compared to samples which did not undergo a water/ethanol wash for PVP removal with samples which did, a big shift is noticed between the resistance numbers after annealing.

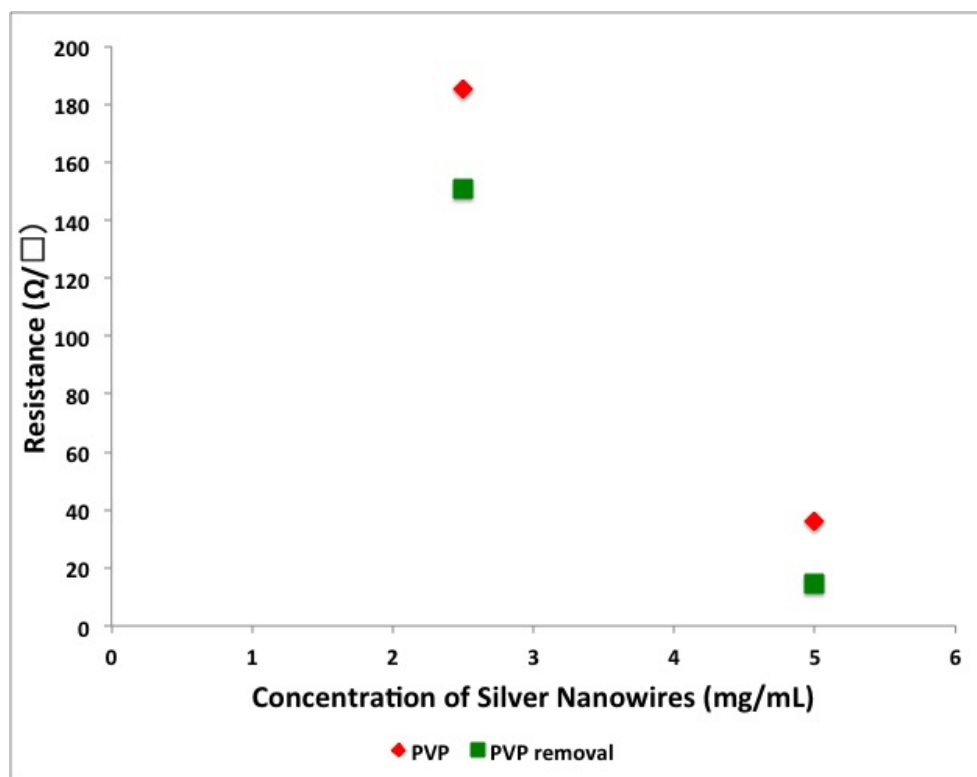


Figure 2.19: Resistance comparison for transfer paper with and without PVP removal treatment

After annealing the coating on the transfer paper, the transfer paper is pressed under the roller at room temperature. The same sample was pressed sequentially with decreasing distances between the rollers. The dependence of resistance with the distance between rollers is illustrated in Figure 2.20, with a starting resistance of $14 \Omega/\square$. The ideal pressing distance is found to be 30 mm, as this is the distance, which resulted in the lowest sample resistance. It is also good to note that pressing the NWs into the polymer coating of the transfer paper makes the coating less prone to a big resistance shift when transferred onto the fabric.

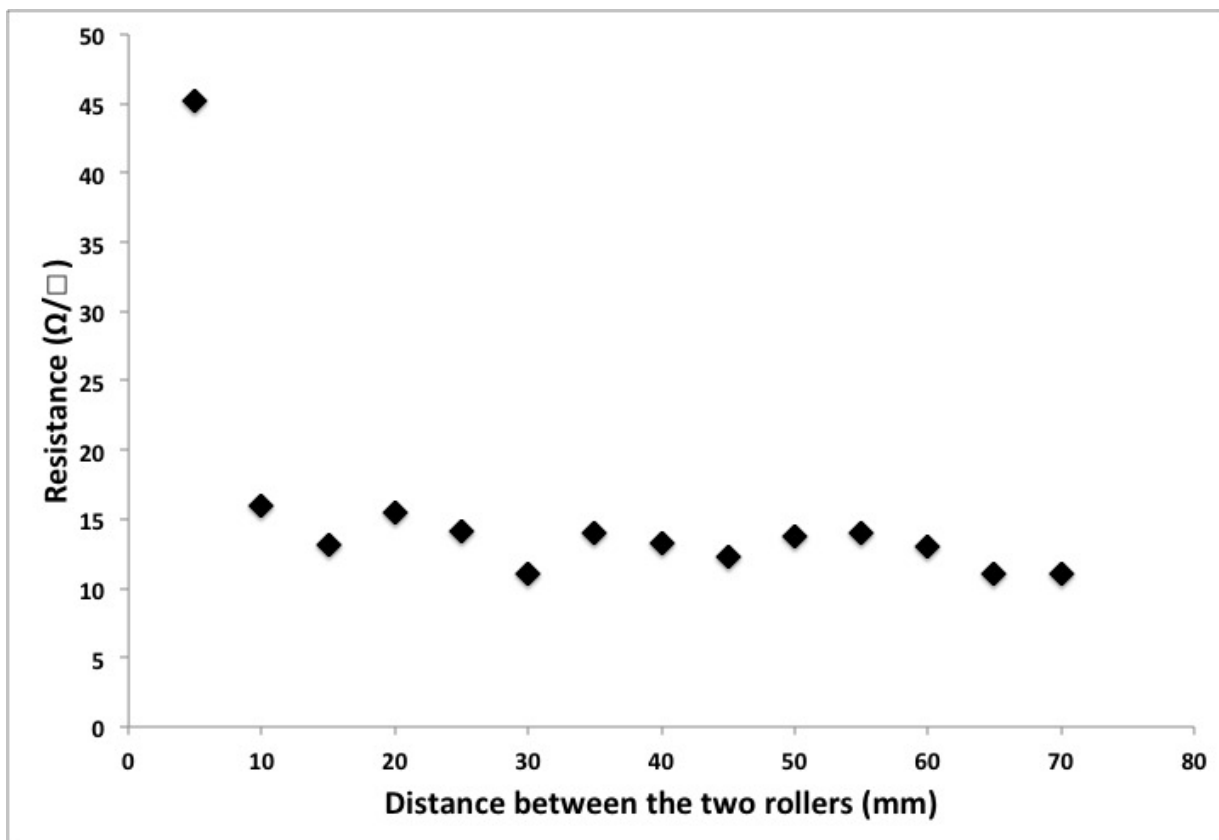


Figure 2.20: Resistance of a silver nanowire coating on transfer paper (initially at 14 Ω/\square) after being rolled at sequentially smaller distances between the rollers.

For NW welding, using a DC current method is not useful when working with low resistance numbers, especially when using constant current. For example, for a 5 mg/mL (4 coats) sample, the resistance on the transfer paper initially is at 5 Ω/\square . Figure 2.21 shows that with change in the current supplied, anywhere in the range of 100 - 500 mA, there is no decrease in resistance observed. And at 700 mA, the resistance jumps to 45 Ω/\square likely due to the high current causing breakdown.

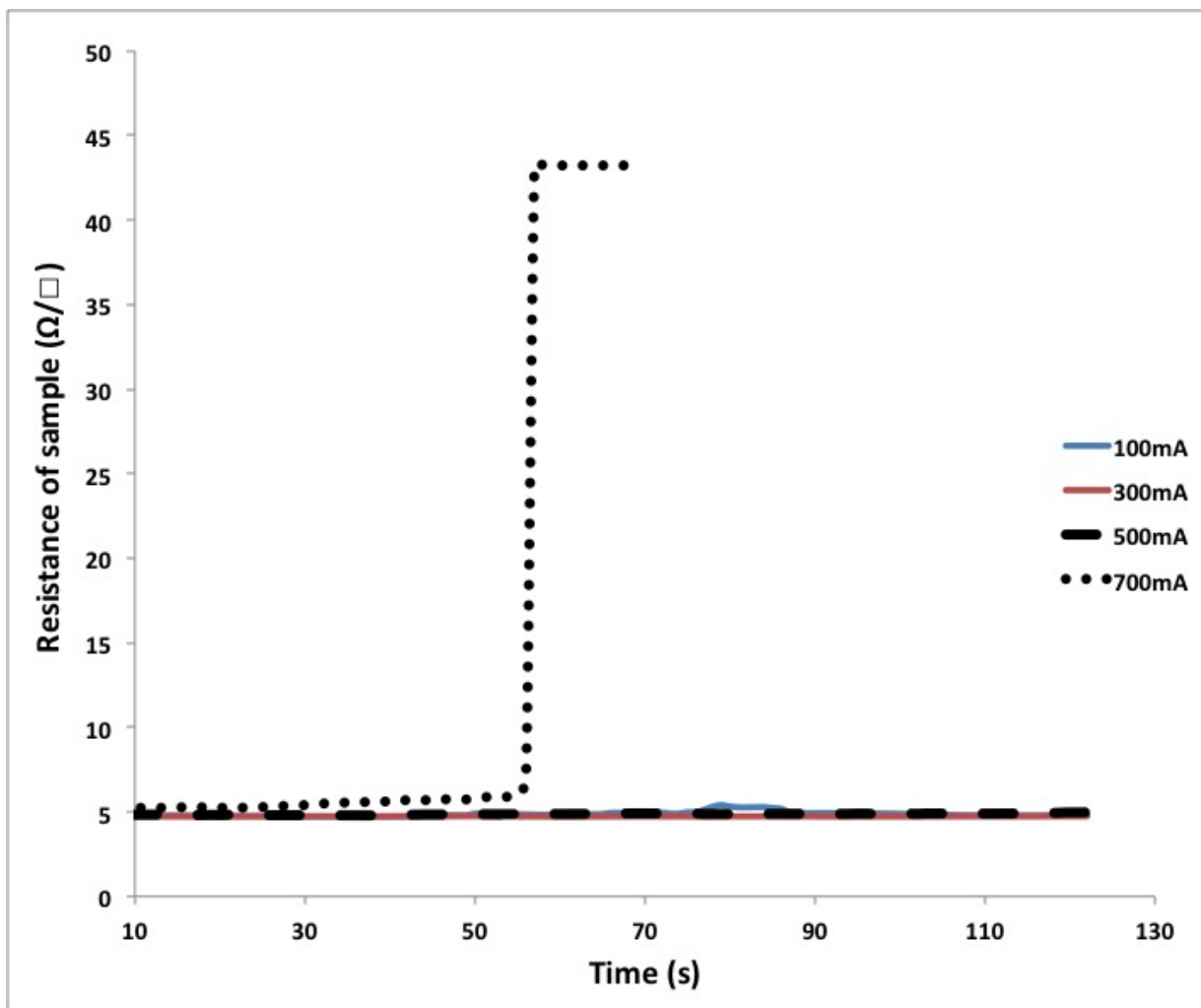


Figure 2.21: Change in resistance of transfer paper coated AgNW sample with constant DC current supply ranging from 100 mA- 700 mA.

Another method is tried to decrease the junction resistance by passing DC current or voltage in pulses periodically [60]. Here, a 3 mg/mL, 4 coat, AgNW sample is prepared on transfer paper and subjected to periodic voltage pulses of 1 min, where there is a 1 min cool down period after every 1 min of voltage application. As seen in Figure 2.22, there is a decrease in resistance observed for the sample from 1150 Ω/\square to 940 Ω/\square .

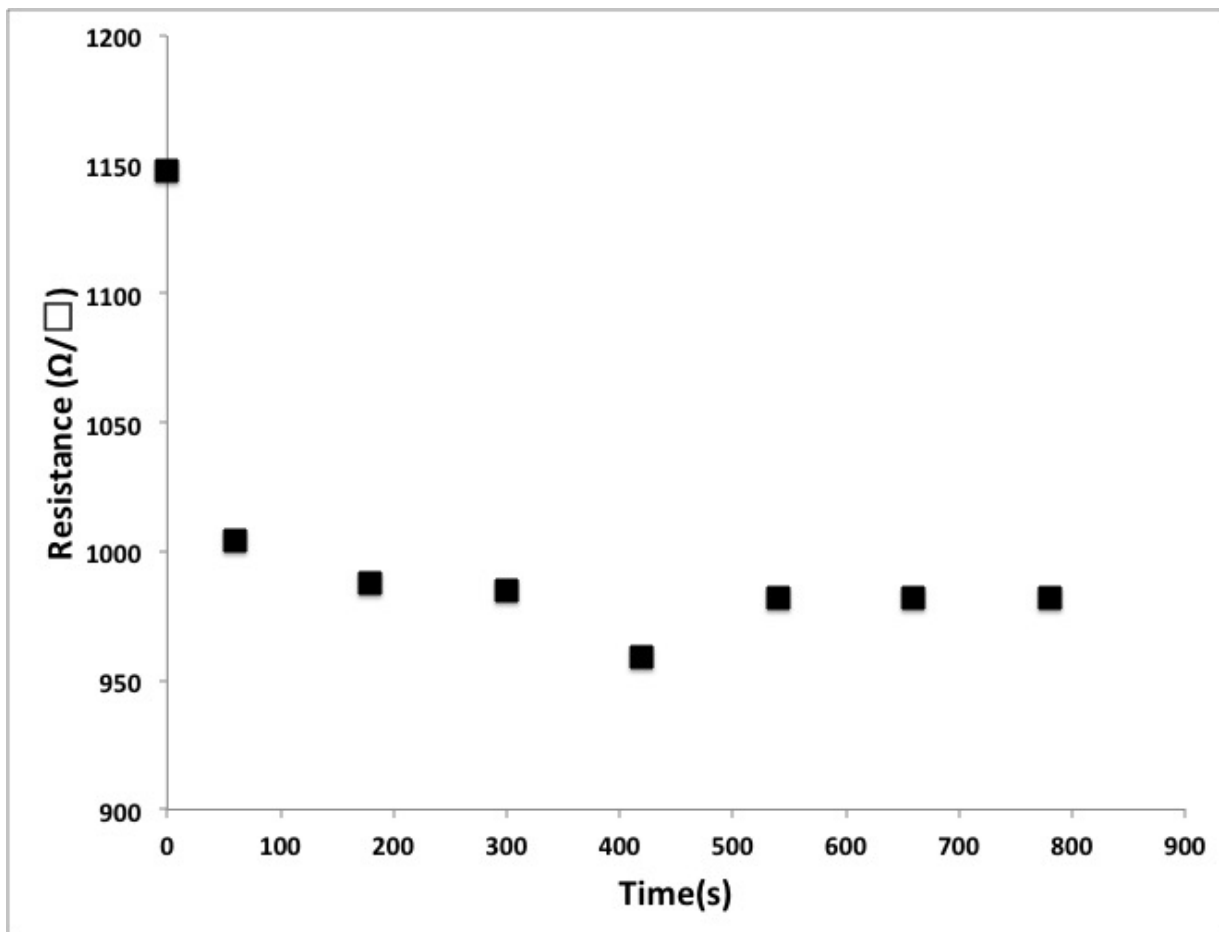


Figure 2.22: Change in resistance of transfer paper coated AgNW with pulsating DC voltage at 29 V.

Because the DC power supply either does not change the resistance or only decreases it slightly, this process was not employed for lowering AgNW coating resistance.

PVP removal using ethanol/water treatment before the anneal and roller pressing of the sample after annealing are all used in conjunction to reduce the junction resistances

for the AgNW coated transfer paper.

Transfer printing optimization

Figure 2.23 shows the resistance of the NW film on various transfer papers. These numbers are obtained from the transfer paper, before the transfer is done on fabric. The annealing temperature varies depending on the transfer paper used, and each transfer paper has a different heat tolerance. CL140 shows the least resistance but it did not transfer well to fabrics. CL120, which has the second lowest resistance, transferred well onto all fabrics tried. Of all papers, CL120 has the least amount of heat tolerance at 90 °C, but SEM imaging showed that it has fairly low roughness. Also, for CL 120, if the anneal is started at 90 °C and gradually the temperature is increased to 120 °C over the 60 mins annealing period, the transfer paper does not burn. This allows for AgNW films to be annealed at a higher temperature and results in low resistance numbers overall. Therefore, CL120 was chosen as the final transfer paper.

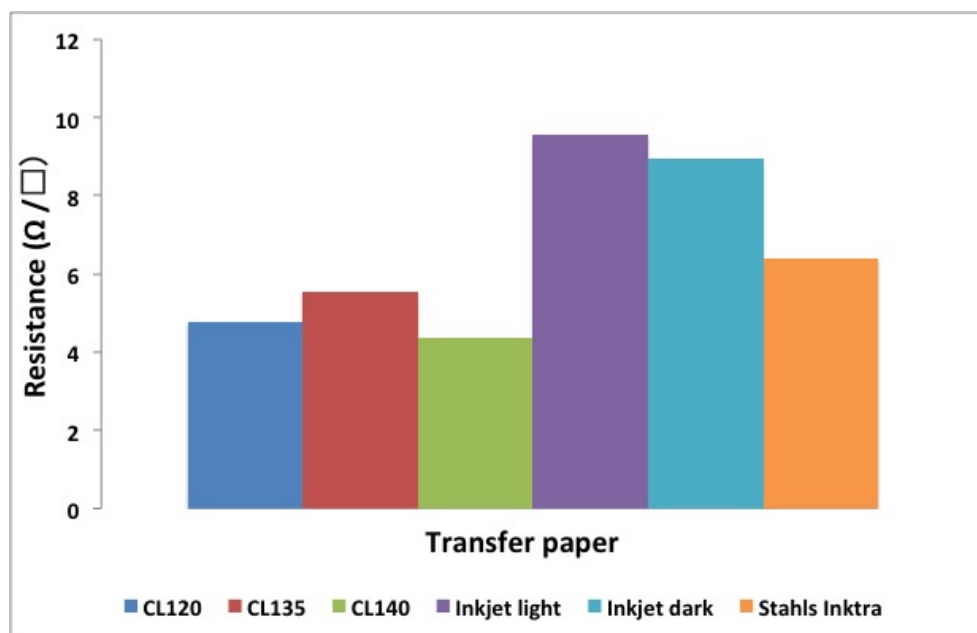


Figure 2.23: Resistance of nanowire coatings on different transfer papers

During the heat pressing step, for temperatures lower than 190 °C no resistance numbers are measured after transfer. This happens because the release of the polymer from the backing paper is not complete, leaving some NWs stuck to the transfer paper. For temperatures above 190 °C, the NWs and adhesive transfer well on the fabric, but the resistance of the sample is high. This may happen due to burning of the polymer present on the transfer paper, which in turn reduces the adhesion of the polymer to the fabric and also might cause disruption of the NW film due to polymer deformation. The final transfer temperature used for all subsequent transfers is 190 °C. The paper transferred well and this pressing temperature resulted in the lowest sample resistances.

Regarding pressing time, at 20 s, the polymer is not entirely detached from the transfer paper, which causes poor transfer. For times 60 s and above, the polymer burns but the

transfer is complete. A burning smell is the evident when the heat press is used for this length of time. The deformation of the polymer causes the NW network to disrupt thereby increasing the resistance. Both 30 and 45 s worked well, but the resistance numbers observed were best for 30 s transfers.

In terms of pressure used to press the transfer paper onto the fabric, medium pressure (as defined by the pressing machine) is required. At high pressure, the transfer paper shows tears and rips, resulting in no resistance being observed upon transfer. At low pressure, the polymer along with the NW network is not completely transferred onto the fabric.

Regarding peeling time, if the peel off of the backing paper occurs right away, when the sample is still hot from the transfer, the transfer is incomplete on the fabric and some areas of the NW network do not transfer. If the peel off time is over 60 s, when the transfer is cold, the peel off does not happen since the backing paper sticks too well to the EVA. The ideal peel off time, with a slow peel off speed, is about 30-50 s.

The resistance for the sample is measured at three times during the transfer process - once on the transfer paper, next when the transfer is sticking to the fabric before the peel off and lastly when the peel off is done and the entire pattern is transferred onto the fabric. Figure 2.24 shows the change in resistance of NW films on transfer paper vs. before and after peeling off the transfer paper.

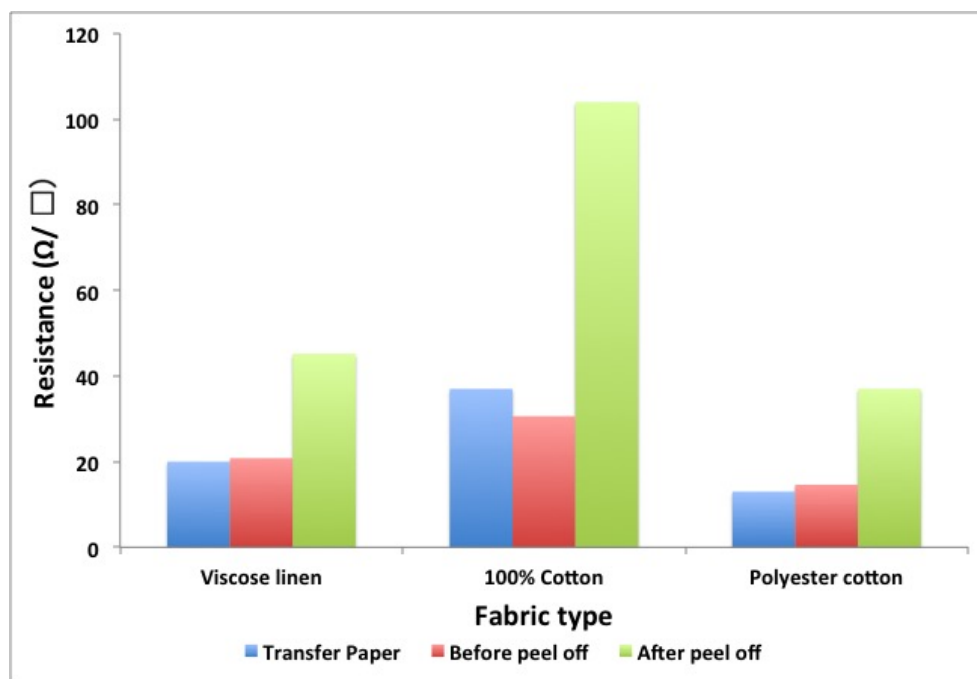


Figure 2.24: Resistance of the silver nanowire films during the different stages of the transfer printing process.

As can be seen in Figure 2.24, the resistance of the NW film on the transfer paper is comparable to the resistance of the NWs on the fabric before peel-off. However, the resistance increases at least 2 - 3 times after the backing paper is removed. The removal of the paper likely causes some of the NW network to distort out of plane due to the pulling force. This breaks some junctions and increases the sample resistance. Altering the peel-off speed could not prevent this jump in resistance.

The number of coats of AgNW films on the transfer paper is an important parameter to be considered. If the NW coating is too thick (at or above 20 mg/mL concentration of AgNWs with 4 coats), I found that transfer onto the fabric is not possible. This is

because there needs to be sufficient space between NWs for the polymer adhesive to pass through so that there is direct contact between the polymer and the fabric. The SEM images in Figure 2.25 show a lower density NW film on transfer paper before and after annealing. The image on the right implies that during the anneal, the polymer was able to ooze through the NW network such that some polymer exists on the surface of the NW film. This allows the polymer to stick well to the fabric. If the network is too dense (at or above 20 mg/mL concentration of AgNWs with 4 coats), the polymer is unable to rise through the NW mesh. Since there are no chemical adhesive linkages formed between the fabric and the NW film, a complete transfer is prevented.

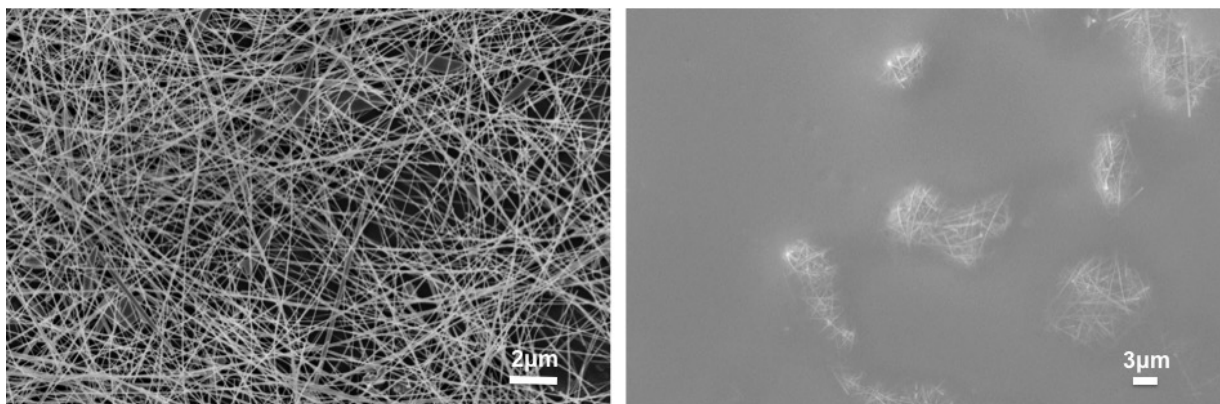


Figure 2.25: SEM images of nanowire coated transfer paper: A. Before annealing B. After annealing

Along with a labmate, Jonathan Atkinson, we screen printed a silver nanoparticle ink on transfer paper and it did not transfer to fabrics at all. This is because, unlike a sparse NW network, the ink forms a continuous film that fully covers the transfer paper surface and the EVA does not contact the fabric. Therefore, NW films provide a unique way to transfer print metal inks onto fabrics, since transfer printing does not work with typical

metal inks.

Once the system is optimized for transfer printing, the NW networks are printed on different fabrics. The three fabrics chosen for NW printing are polyester-cotton, 100% interfacing cotton and a viscose-linen blend fabric. Figure 2.26 shows images of the different fabrics when coated with AgNWs using the same parameters. Interfacing cotton shows the highest resistance among the three samples of fabrics used. The peel off after transfer printing is uneven and blotchy in certain sections.



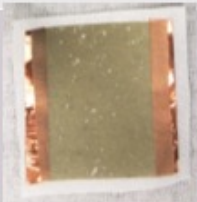
#	Fabric	Image	Resistance (Ohms/ \square) (5mg/mL AgNWs in ethanol)
1	Polyester Cotton		42
2	Viscose Linen		39
3	100% Interfacing cotton		60

Figure 2.26: AgNW coating on different fabrics

Figure 2.27 shows a magnified section of the uneven, blotchy transfer onto the interfacing cotton fabric. These white areas on the transfer, where the NWs do not stick to the

fabric, is where the transfer was not possible. Because not as many NWs transferred to the interfacing cotton compared to the polyester and viscose, there are not as many NWs available for conductive and this likely explains the increased resistance.

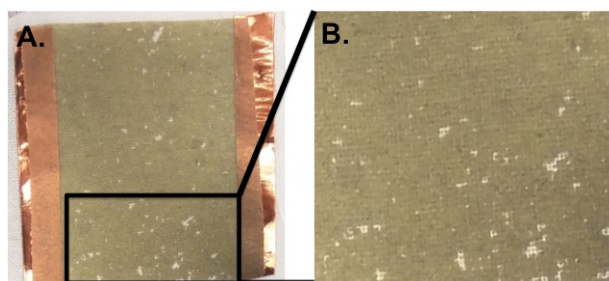


Figure 2.27: Zoomed in AgNW coating on interfacing cotton

As seen in Figure 2.28, the thickness of the threads for each of the fabrics is different and so are the gaps between the interwoven threads. Comparing the different fabrics, the large spaces present between the thread of the interfacing cotton, could be causing the transferred polymer to not have as much surface area to attach to, thereby leading to a poor transfer on the fabric.

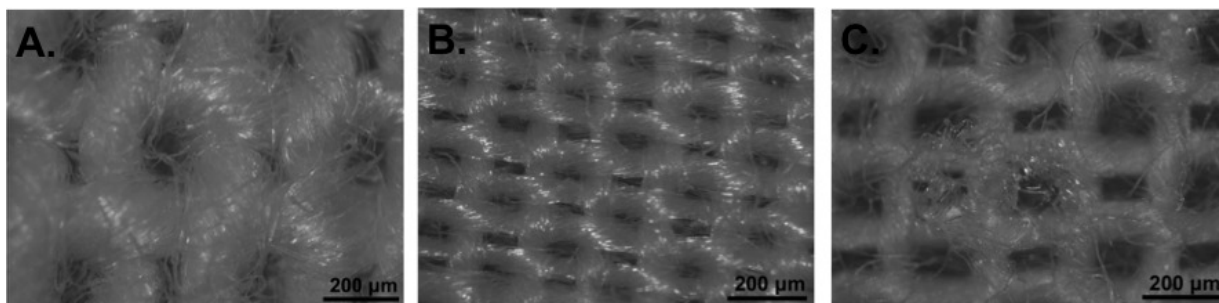


Figure 2.28: Optical microscopy images of fabrics A. Viscose linen B. Polyester cotton C. Interfacing cotton.

The optimal transfer printing process found in this work is summarized in Table 2.8.

Table 2.8: Final optimized parameters for transfer printing

Parameter	Number
Transfer paper	CL 120
Annealing temperature	120 °C
Number of coats	4
Heat press temperature	190 °C
Heat press pressure	Medium
Heat press time	30 s
Peel off time	40 s
Fabric used	Polyester-cotton

Electrical characterization and cost

Figure 2.29 establishes the correlation between the amount of AgNWs used with respect to the resistance of the sample, as well as the material cost of the NWs used. As expected, the resistance increases as the density of AgNWs decreases.

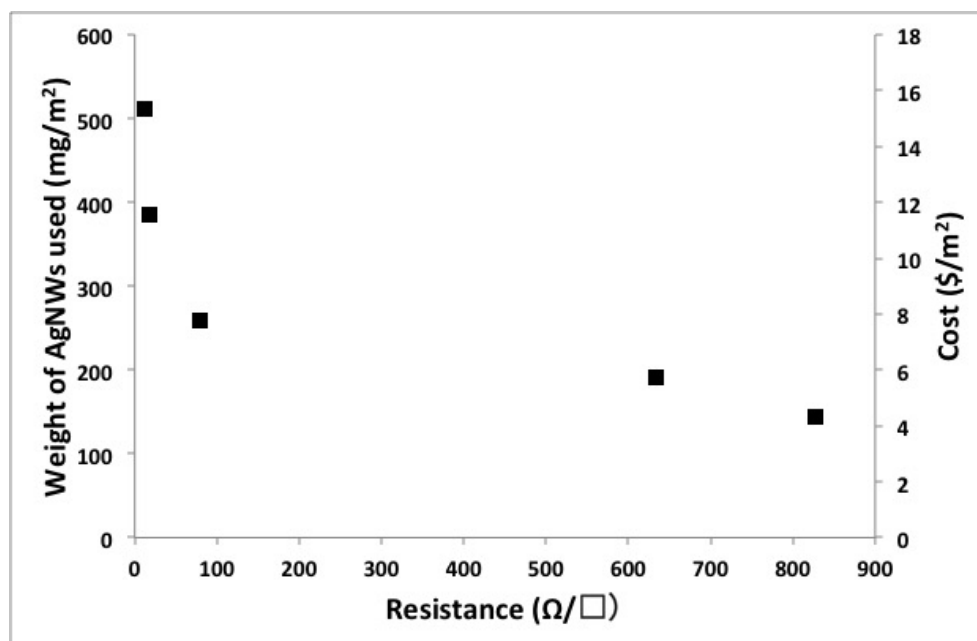


Figure 2.29: Resistance comparison for different densities of AgNW coatings along with material cost estimates.

As it can be seen in Figure 2.29, the cost of printing AgNWs using transfer printing is fairly low. Compared to dip coating, where the cost of coating the fabric to achieve a resistance of $30 \Omega/\square$ is at $\$ 700/\text{m}^2$, using transfer printing, it costs $\$ 16/\text{m}^2$. And because less AgNWs are used the coating is also lower weight.

Mechanical testing - bending and folding tests

Figure 2.30 shows the results of the bending test. The fabric is held around a rod with a 60 mm radius for 60 s, then unfolded. Immediately after unfolding the resistance is fairly high, but after 60 s the resistance stabilizes and the measurement is taken. After 20 cycles of bending, there is a 7% change in resistance of the sample.

As seen in Figure 2.17, the AgNW film is in direct contact with the fabric once transferred and covered on top with the EVA polymer. When the fabric coated with silver nanowires is imaged under a SEM, the only layer visible is of the EVA and not the silver nanowire film. SEM of the NWs on fabric is not possible due to the EVA coating on top of the NW film and thus SEM could not be used to investigate the fabric samples in Figure 2.26, 2.31 and 2.36.

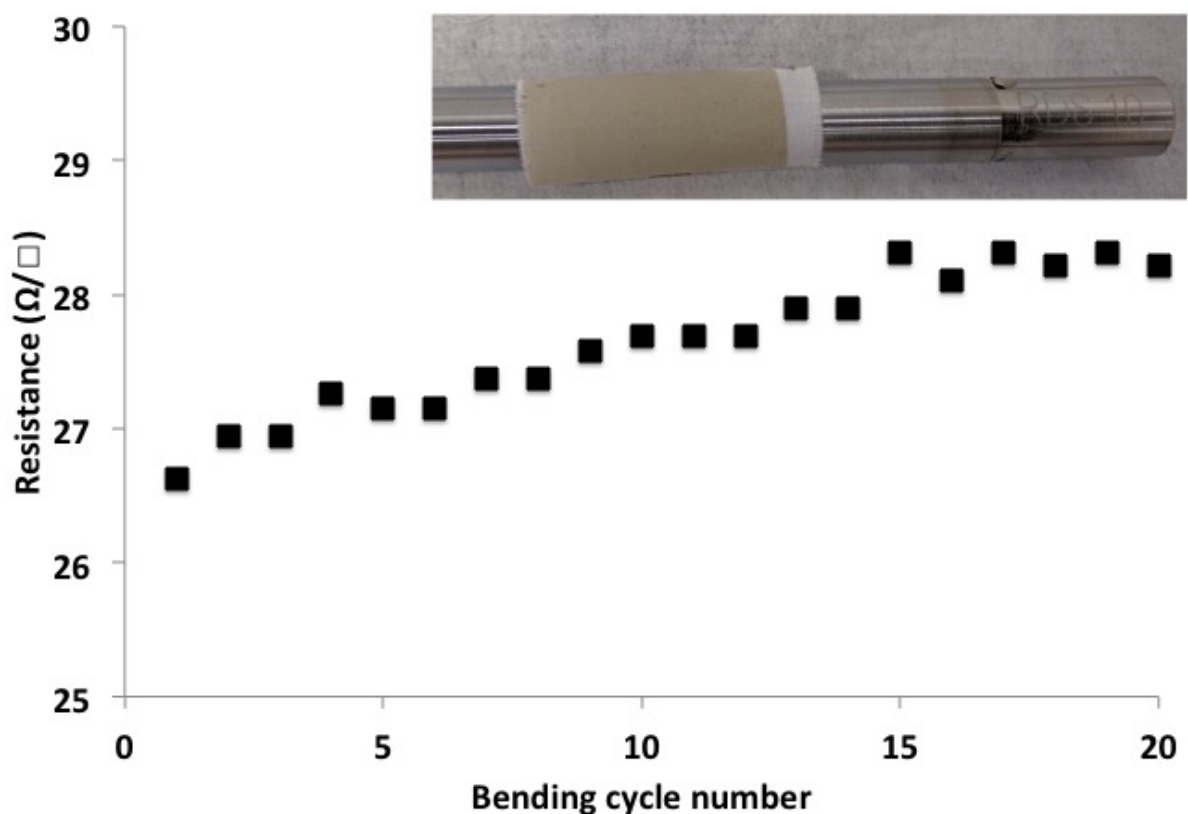


Figure 2.30: Bending test with AgNW transfer printed fabric. The inset figure shows the bent nanowire coated fabric sample around a rod with a 60 mm radius.

For the folding tests, the conductive fabric is folded in half and held in place for 60 s.

After this, the fabric is restored to the flat state and the resistance is measured. As seen in Figure 2.31, the change in resistance after 10 folding cycles is 10%.

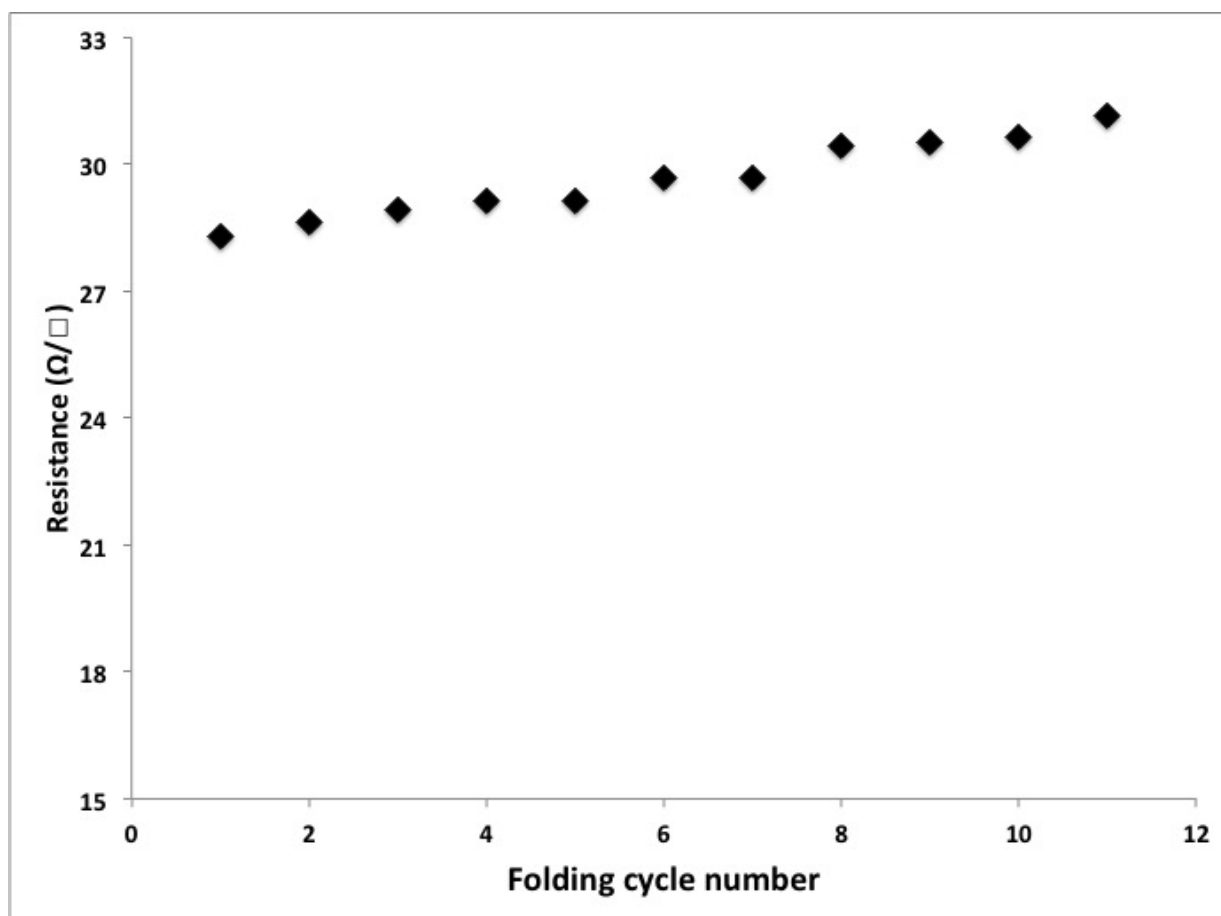


Figure 2.31: Folding test with AgNW transfer printed fabric

For the square folding test, the fabric was bent once in x-direction and then in y-direction and held for 60 s each. The change in resistance is shown in Figure 2.32. The increase in resistance is higher compared to the basic bending and folding tests, due to the fact that some NW networks might be broken due to multiple bends at the same time,

causing the resistance to increase 53% after 10 folding cycles.

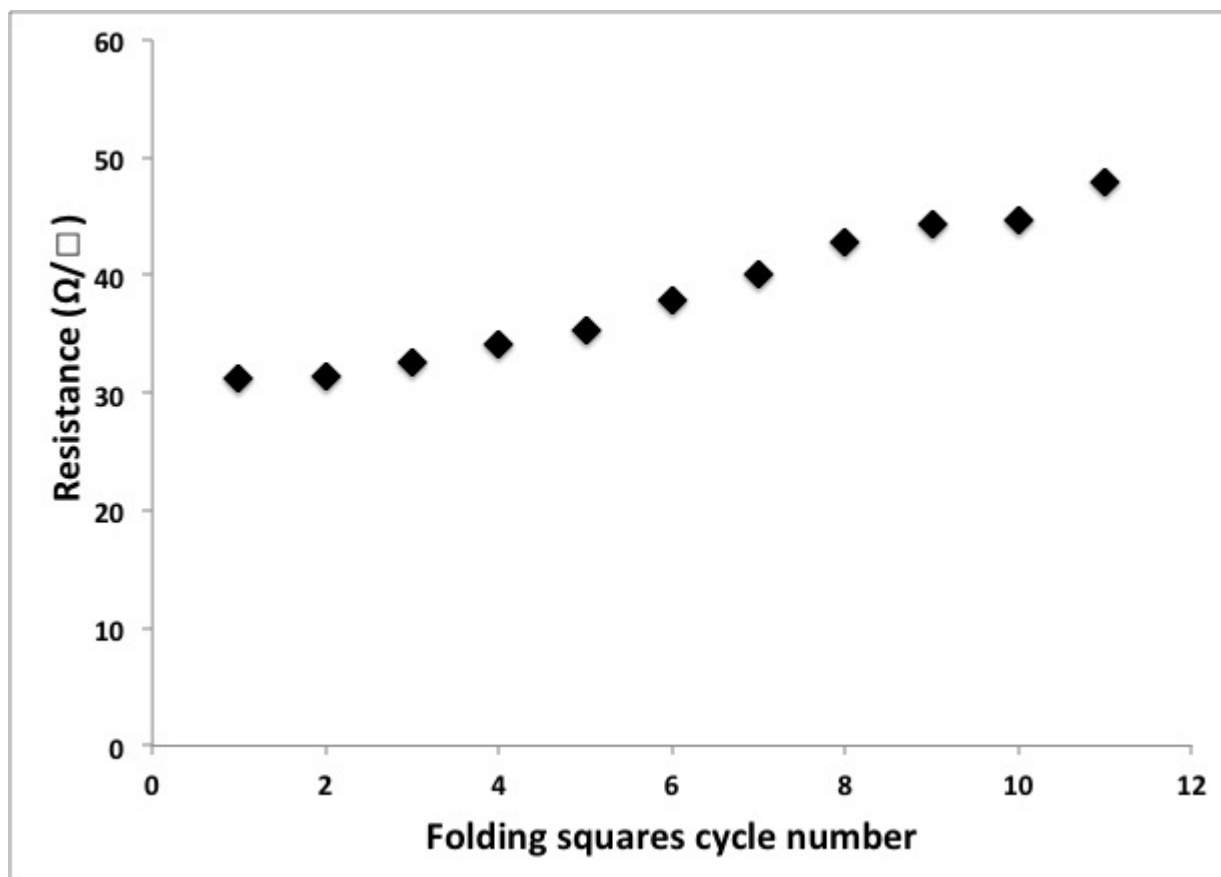


Figure 2.32: Folding square tests with AgNW transfer printed fabric

Transparency comparison tests

To quantify the transparency of the AgNW films on fabric, a spectrophotometer is used. The three different techniques used to measure the transparency of the film are:

1. Measure the transmittance through the fabric with and without AgNW coating

using a spectrophotometer. Since the fabric is actually opaque, the measurement is not feasible.

2. Measure the transmittance of the transfer backing paper coated with and without AgNWs using a spectrophotometer. The transfer paper is also opaque, which does not allow for the spectrophotometer to quantify the transparency of the sample. The polymer film is the only element of the transfer paper that actually transfers onto the fabric along with the AgNW film. And since no measurements can be made on fabric or transfer paper, one is unable to quantify the transparency of the AgNW film.

3. The AgNW coating is applied on PET using the Mayer rod coating technique. For PET itself, the transparency is 89.3 % at a wavelength of 550 nm. When a $10 \Omega/\square$ AgNW coating is applied to the PET, the transparency decreases to 23.3%. This means that the transparency of the coating was 44% which is quite low.

Visual observations were done on the nanowire coated fabric. Figures 2.33 and 2.34 show a NW film transfer printed on color-printed cotton samples. The resistance of the coatings were $100 \Omega/\square$. The images show that the transfer printed films do not drastically change the colour of the textiles, and the pattern of the textile can still be seen. Commercially available conductive fabrics, as shown in Figure 2.35, are either copper, silver or black since the coating is not transparent. The NW film transfer printed on the fabric however is quite transparent. By my knowledge, this is the first conductive coating for fabrics that is transparent. If the process parameters of the NW deposition, transfer paper and the transfer printing process are further optimized, it may be possible to increase the transparency of the NW coating and thus seamlessly impart conductivity to a fabric.



Figure 2.33: NW coating on cotton patterned fabric The left image shows the fabric without the NW coating and the right image shows the fabric after NW coating



Figure 2.34: NW coating on cotton patterned fabric The left image shows the fabric without the NW coating and the right image shows the fabric after NW coating



Figure 2.35: Silver coated fabric

Lifetime testing

Lifetime tests are performed with transfer printed samples of AgNWs on interfacing cotton, polyester-cotton and viscose linen fabric. The samples are prepared and left out in air for 30 days and the resistance is measured every 3 days. The samples were coated with 10 mg/mL AgNWs in ethanol solution. As seen in Figure 2.36, the resistance of the each of the fabrics coated with AgNWs increases by 21%, 43% and 120% in the first 6 days for polyester cotton, interfacing cotton and viscose linen respectively. For viscose linen fabric, an interesting jump in resistance is observed between day 6 - 15, but then it stabilizes to the same number as the resistance on the 6th day. This resistance on day 15 might just be outlier. For both polyester-cotton and cotton, after the 6th day, the resistance does not increase anymore and is constant for the rest of the month.

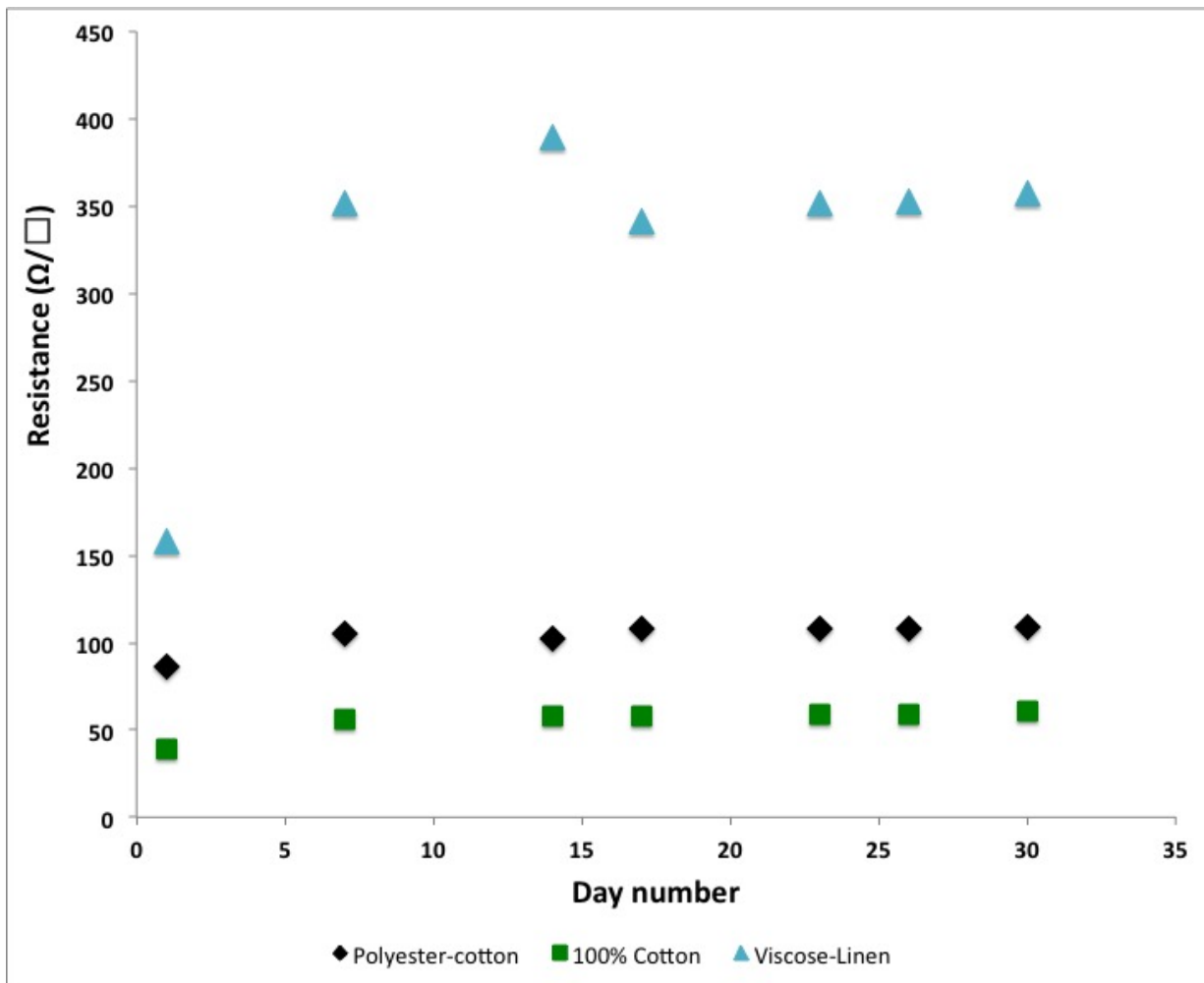


Figure 2.36: Resistance change of AgNW printed fabrics over 30 days for cotton, polyester-cotton and viscose linen fabrics when left in air

One hypothesis which explains the increase in resistance initially is due to the corrosion of AgNW film while being exposed to air. AgNWs are known to corrode in air, specifically due to sulfur containing gases, and this corrosion is accelerated with moisture [53]. Although EVA degrades in oxygen and water, depending on if it is cured or uncured, it is fairly stable [61]. Since the EVA is annealed with the AgNW film on the transfer paper,

it is cured and should not degrade super fast. Moon et al. [62] have shown that the sheet resistance of AgNWs coated on a PET substrate when exposed to air for 30 days change in resistance from 25 ohms/square to 70 ohms/square. This is a 180 % jump in resistance over 30 days. Compared to these results, AgNWs on a variety of fabrics show an increase in resistance from 20% to 120% over 30 days, which is lower than AgNWs on PET tested by Moon et al. This supports the fact that the presence of EVA through the NW network, both below and above it, might be helping with reducing corrosion. Although the NW coated fabric does not undergo corrosion very fast, passivation solutions may be required for longterm usage.

Washing tests

Washing tests are performed using samples coated with AgNWs with concentrations of 10 mg/mL and 20 mg/mL. The three different kinds of washing tests performed are:

1. Sample is immersed in distilled water for 15 mins.
2. Sample is immersed in detergent and distilled water at room temperature for 15 mins followed by washing with distilled water.
3. Sample is immersed in detergent and distilled water at 40 °C for 15 mins with a magnetic stir bar rotating at a speed of 30 rpm.

For all of the above experiments, no resistance was observed after the experiment was completed. The AgNW network is embedded into the EVA polymer of the light transfer paper and EVA is well known to degrade and release acetic acid when exposed to water [63] [64]. In the literature, AgNW coated threads by Atwa et al. [51] were washed with minimal resistance effects. Therefore, perhaps the catastrophic resistance changes seen here have something to do with the AgNW network being embedded in the EVA polymer.

EVA is well known to degrade and release acetic acid when exposed to water and this could somehow have a negative effect of the NW network. More experiments and analysis need to be done to determine the reason why washing severely degrades conductivity. It is clear that the NW film needs to be encapsulated on both sides of the fabric to make slow down the degradation. Some materials that are used for encapsulation of metals on fabric include silicone and epoxy.

Dark transfer paper results

For a 10 mg/mL AgNW coating, with 4 coats of AgNWs on both dark and light transfer paper, the resistance numbers are similar and close to $10 \Omega/\square$. But when both the transfer papers are transferred onto the fabric, the dark transfer paper retains the resistance. The resistance for the AgNW film, when transferred from the light transfer paper onto the fabric, increases to $80 \Omega/\square$. Although the dark transfer paper is able to provide lower resistances and works for all fabric types, the NWs may be less protected from mechanical rubbing and degradation in air. Also, the transparency of the NW film achieved is lower compared to light transfer paper as can be seen in Figure 2.37. The transparency for dark transfer paper is lower because of the presence of an opaque cross-linked polymer and an opacifying material [57].



Figure 2.37: Transparency comparison between light and dark transfer paper. The first panel is a regular printed cotton cloth. The second panel is a printed cotton cloth coated with AgNW network using light transfer paper. The third panel is a printed cotton cloth coated with AgNW network using dark transfer paper.

Dark transfer paper allows the nanowire conductive coating to be directly accessed to make a conductive pathway and connections such as copper tapes are not needed (shown in section 3.3). Although dark transfer paper does not encounter the problem of peeling stress as the light transfer paper, it cannot be transparent, due to the opaque backing present on the dark transfer paper.

2.6.5 Conclusion

Results described in this chapter prove that the existing techniques used to coat NWs onto fabrics have several drawbacks and there is a need for a better technique in order to reduce costs for making conductive fabrics. The dip coating technique, which is the only technique shown in previous works to coat AgNW on fabrics, has shown low resistance for samples due to the high amount of silver used. Dip coating and brush coating are easy techniques used to coat fabrics with AgNWs, but have issues of high cost due to the high amount of silver used, non-uniformity of the coating and the requirement for surface modification

of fabric for NW adhesion. Transfer printing shows promise in terms of printing metallic NW inks onto fabrics. Apart from being cost effective and an industrially compatible technique, it offers the unique advantage to produce fairly transparent conductive coatings on the fabrics. It was shown to work for both natural and synthetic fabrics without the need for surface modification. It can be applied to textiles after they are manufactured (i.e. printing does not have to be done at the time of textile manufacturing such as would be the case for dip-coating or using conductive threads). The nanowire coating is quite mechanically flexible, and can have minimal resistance change (26% for polyester-cotton) after being left in air for 30 days. With a series of applications explained in Chapter 3, along with several other future options, the transfer printing of AgNW films onto fabrics proves to be a promising technique with the potential to be used for printing other metallic NWs and carbon nanotube as well.

Chapter 3

Applications of transfer printing

In Chapter 2, transfer printing was shown as a credible technique to produce conductive AgNW coatings on fabrics. The applications that these nanowire film coatings are tested for in this chapter include patterning on fabrics, constructing LED circuits for apparel fashion, electromagnetic interference (EMI) shielding and the ability of the conductive fabrics to generate heat when a voltage is applied.

3.1 Patterning on fabrics

Patterning a conductive coating as tracks or pads is required for many device applications. Furthermore, to a compared coating the entire fabric surface, it uses less metal and is therefore less cumbersome, and allows the majority of the textile to retain its softness and breathability. A few methods exist to define conductive patterns on fabrics. Defining patterns using brush coating does not result in sharp patterns. In screen printing a mask is required, which is an extra cost, and the rheology of the ink is limited to a certain range

otherwise the ink bleeds underneath the mask edges. Another method to make conductive tracks is to weave in conductive threads at particular locations, but this is time consuming and is preferred to be done at the time of textile manufacture. With transfer printing, patterning is easy, with sharp edges and boundaries obtainable. Coating shapes of desired resistance and transparency can be designed using transfer printing. The methods section below elaborates how the patterning is done and some of the designs generated in the lab.

3.1.1 Methods and results

Once the nanowires are coated and annealed on the transfer paper, the nanowires on transfer paper are put through the Silhouette. The Silhouette machine is a cutter, which is able to receive instructions to cut specific design created in the Silhouette software and cut the shapes accordingly. The smallest feature that can be cut with the Silhouette cutter is 0.5 mm. Once the design is cut, it is transferred onto the fabric using the heat press. As can be seen in Figure 3.1, various designs have been patterned on polyester-cotton fabric. The edges of the patterned nanowire films are observed to be clean and sharp.

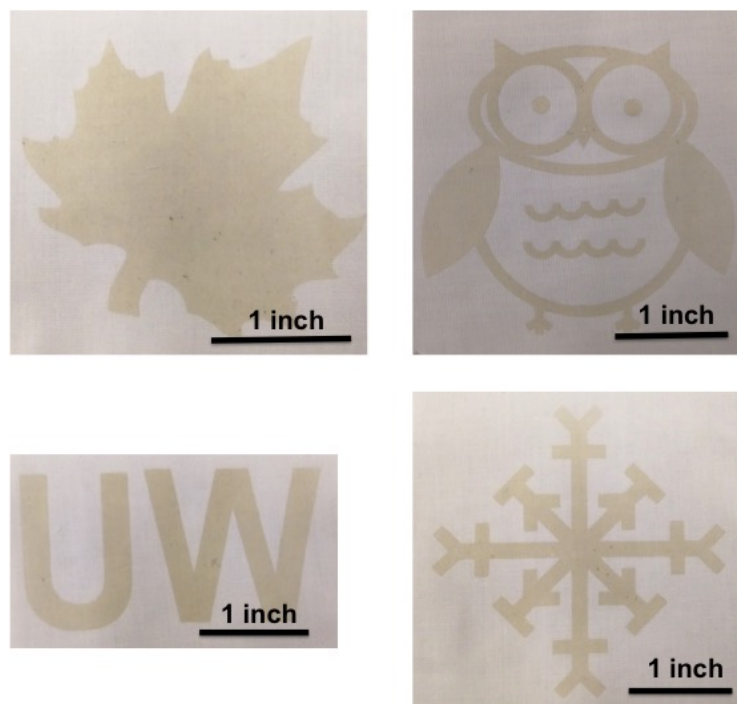


Figure 3.1: Designs of conductive silver nanowire ink patterned onto polyester-cotton fabric using transfer printing

3.2 LED integrated fabric

To demonstrate an application where the printed and patterned nanowire fabric can be used, a demo was composed using LEDs with an adhesive backing and printed AgNW networks. The nanowires are printed and patterned on the fabric. For the light transfer paper, the nanowire film is coated on the light transfer paper, annealed at 120 °C for 60 mins, and then the nanowire film is put down on the fabric, where the NWs are in direct contact with the fabric. The copper tape is put down on the fabric first, which comes in contact with the silver nanowire film when transferred, thereby making contact with the conductive film and completing the connection for the light transfer paper (Figure 2.12

and the transfer process subheading under section 2.6.3 explains how the silver nanowires make contact with the copper tape and complete the connection).

The fabric and transfer paper are then subjected to the heat press (heat press temperature of 190 °C for 30 s) and once the sample cools down, the transfer paper backing is peeled off from the fabric. Since the light transfer paper does not have nanowires exposed at the surface for the connection of electronics, copper tape is used to connect the ends of the network and electronic components. Figure 3.2 shows two simple LED circuits completed using light transfer paper, with and without a patterned circuit.

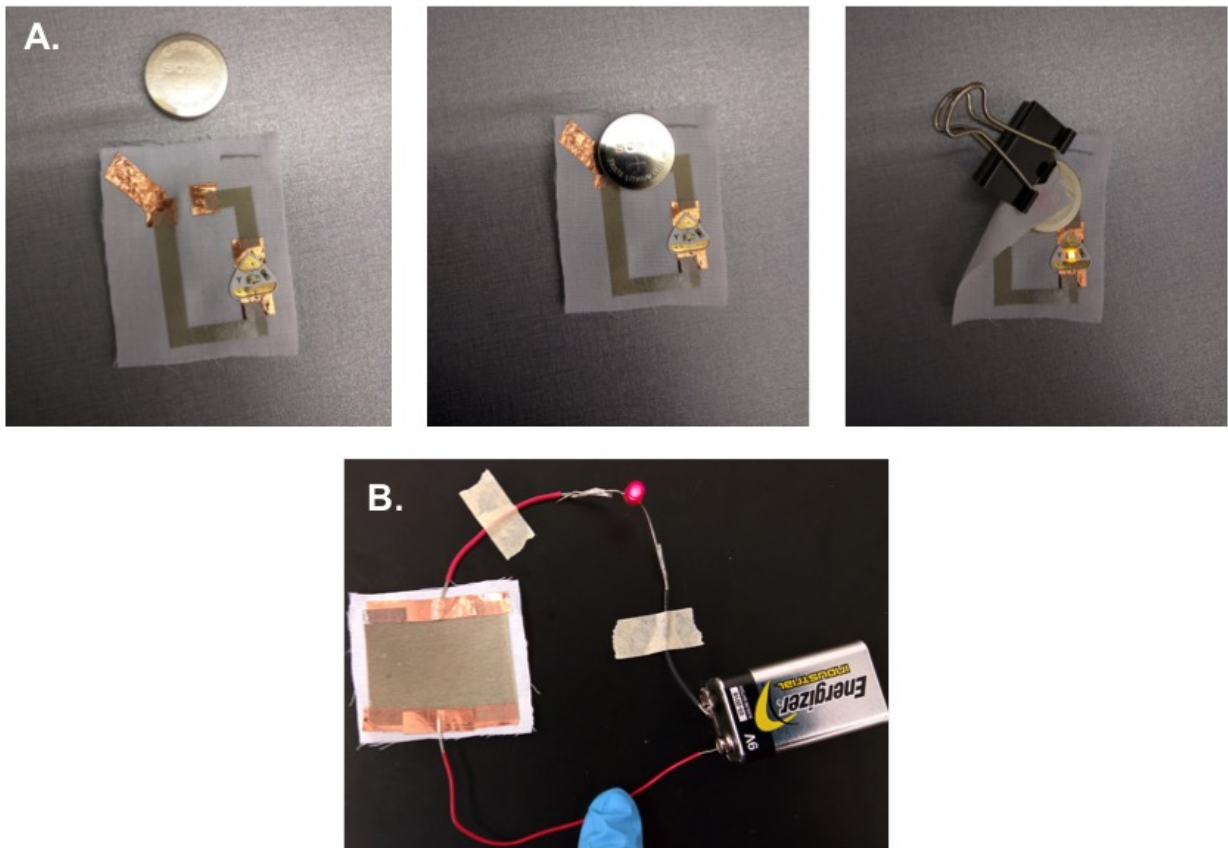


Figure 3.2: Simple LED circuit printed onto polyester-cotton fabric using light transfer paper. A: Silver nanowires are patterned and printed onto the fabric. B: Silver nanowires printed on fabric without patterning

A demo piece built is shown in Figure 3.3. A bracelet is first printed onto polyester-cotton fabric using a color laser printer. A second polyester-cotton fabric piece, the back-end, is made by patterning the AgNWs on fabric using dark transfer paper and stick-able LEDs. The NW film is peeled off from the transfer paper backing and attached to the fabric using the heat press at 375 °C and a 30 s press for dark transfer paper. Using a dark transfer process instead can avoid using copper tape since the conductive nanowire film is exposed on the top surface of the fabric. Therefore, the LEDs can directly contact the

nanowire film. A 3V coin battery was used to power the LEDs. The bracelet-patterned fabric sample was placed on top of the LED circuit so that the NW pattern is hidden while the light from the LEDs could still be seen.

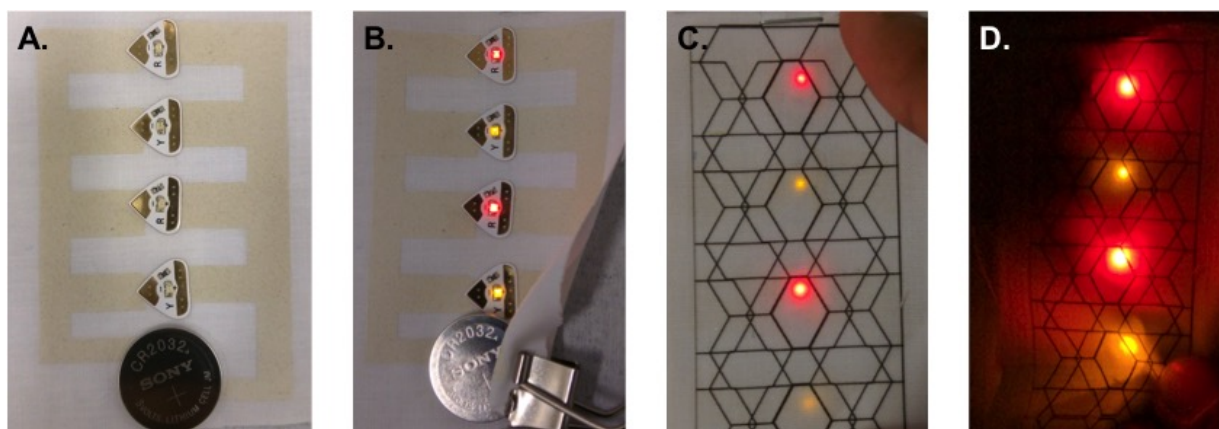


Figure 3.3: Design with LED. A: Patterning of nanowire-coating interconnects on polyester cotton with LEDs. B: Circuit completed with a coin battery. A second fabric sample is laid over the LED circuit to hide the patterned interconnects with both light (C) and dark (D) room lighting conditions.

This demonstration shows that AgNW inks can be screen printed into arbitrary shapes with sharp edges without the use of a mask. It can also be done post-textile-manufacture. Such patterns could even be printed at home with the use of a hand iron.

3.3 Electromagnetic interference shielding

An electromagnetic (EM) wave has 2 components - an electric field and a magnetic field, which are perpendicular to each other. Electromagnetic interference (EMI) refers to the pollution caused by unwanted radiation generated by electronic and telecommunication

devices. EMI shielding is the phenomenon of protecting humans and electronics from this pollution by using materials that can block EM waves. EMI shielding finds applications in various industries like automotive, aerospace, defense and household goods. These EMI shielding materials need to be conductive, thereby possessing mobile charges. These charges then interact with the EM wave and help dissipate the energy. Several materials like graphene [65] [66], carbon nanotubes [67] [68] and metallic nanowires [69] [70] are used combination with polymers (via blending or coating with the substrate material) to produce EMI shielding materials. AgNWs are of high interest because of their high conductivity and high aspect ratio for applications in EMI shielding. A high aspect ratio (aspect ratio= length/width of sample) [71] is critical for achieving a high shielding effectiveness (SE) because they lead to longer conducting pathways in a random network, thereby increasing the conductivity of the sample. A high conductivity is necessary to disperse electrons throughout the sample to achieve a high SE.

Previously, AgNW blended with a variety of polymers have shown exceptionally good EMI shielding, even when compared with other nanomaterials like carbon nanotubes. Work done by Sundararaj et al. shows EMI shielding of AgNWs and MWCNT composites with polystyrene (PS) [70]. The AgNW/PS composite shows about 30 dB of shielding at X-band frequencies with a nanofiller loading volume of 2.5% compared to the MWCNT/PS which only show about 20 dB of shielding at the same loading volume. For AgNW/polyimide composite foams, the work done by Wang et al. shows 772 dB/g.cm³ of shielding at 800 - 1500 MHz [72]. Another work by Wang et al.[73], shows shielding effects of 20 dB for the frequency of 3 - 17 GHz for PVA/AgNW and epoxy/AgNW conductive films. This work also compares silver nanoparticle efficiency with AgNW networks and proves that the shielding effect of the nanoparticles is much lower. All these works show

that AgNWs have the capability to block EM waves. For the transfer printed AgNW samples on fabric, experiments are done to analyze their potential of blocking EM waves and to compare the change in shielding with the concentration of the AgNW film coated.

Preliminary experiments were performed using waveguides corresponding to certain AC frequencies. The basic setup of a waveguide experiment is shown in Figure 3.4. The setup consists of 4 main features- a vector network analyzer (VNA) for supplying the current to generate waves at a certain frequency, waveguides to convert electricity into waves of required frequency, right angle coaxial adapters to connect waveguides to the VNA and a computer to record the data.

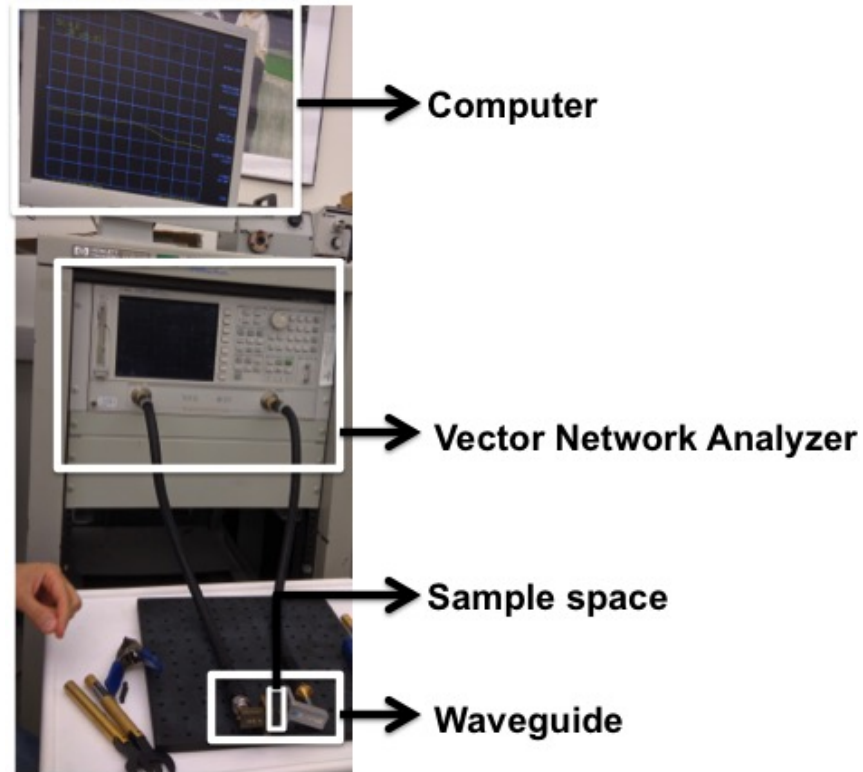


Figure 3.4: Setup using a WR340 waveguide and a vector network analyzer for quantification of EM shielding using silver nanowire coated fabric

The waveguides were connected to the vector network analyzer. The waveguide used has a frequency range of 12.4-18 GHz. The two ports of the vector network analyzer act as input-output response ends. The input is in the form of current, which is converted into AC frequency waves using the waveguide. Depending on the length and width dimensions of the waveguide, the waveguide has a certain frequency range it can generate. The setup is used to measure the amount of EMI shielding in terms of the power loss. The loss is measured in the unit of decibels (dB). Equation 3.1, is used to quantify the loss in power.

$$\textit{Shielding Effectiveness} = 10\log(P_{in}/P_{out}) \quad (3.1)$$

where P_{in} = Incident power and P_{out} = Transmitted power

AgNW transfer printed polyester-cotton fabrics with AgNW densities of 20 mg/mL(4 coat sample), 15 mg/mL (4 coat sample) and 10 mg/mL (4 coat sample) are measured. These samples had resistances of $3 \Omega/\square$, $30 \Omega/\square$ and $90 \Omega/\square$, respectively. The control sample was polyester-cotton fabric without a coating.

Figure 3.5 shows the power loss exhibited by the non-conductive fabric and the AgNW coated samples with different AgNW densities.

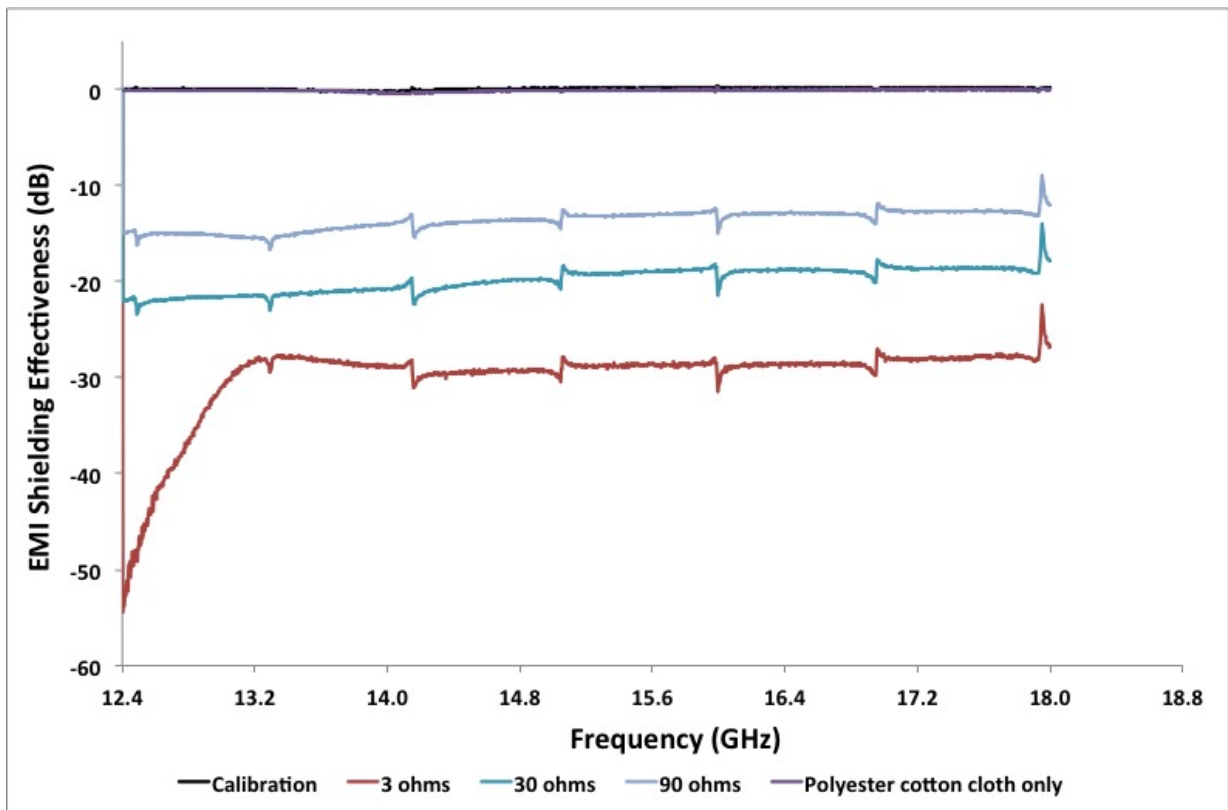


Figure 3.5: Two port experiment with 12.4-18 GHz waveguide for measuring loss of transmission for silver nanowire coated fabrics with different density of nanowires

With the fabric only sample, it is observed that the RF loss is at 0 dB and overlaps with the calibration curve. This shows that the polyester-cotton fabric by itself does not block any radio frequency (RF) waves. With the 20 mg/mL fabric, there is a loss of 30 dB, for 15 mg/mL, the loss is 20 dB and for the 10 mg/mL fabric the loss is 10 dB. These results show that AgNW printed fabrics are capable of blocking EM waves. And with the transfer printed fabrics, depending on how much blocking is required for the application, one can design a fabric with the required conductivity.

3.4 Joule heating

Joule heating is the process where electricity is converted into heat through a resistive element. Joule heating is used in several applications in the real world, which require fabric-based heating processes, including uses in the apparel industry (heated garments and gloves), automotive (car seats), household use (heated floors and walls) and the medical industry (electrotherapy treatment and heated blankets). Work done by Khaligh et al. [74] and Atwa et al. [51] shows that AgNW coated PET and threads, respectively, show Joule heating. Here, the transfer printed AgNW fabrics are tested for their Joule heating capability and to quantify and relate the AgNW resistances and Joule heating effects.

The AgNW coated fabrics are tested for the change in temperature of the fabric using a range of voltages between 1 V and 10 V. The samples tested for Joule heating were polyester-cotton and cotton coated fabrics with variable AgNW concentrations. The samples are square with lengths and widths of 4 cm each. The concentrations of the AgNWs used were 5, 10 and 20 mg/mL. The setup for the Joule heating experiments is shown in Figure 3.6. A thermocouple is attached to the fabric sample on the top of the coated

fabric to record the temperature change, which is tracked by a multimeter connected with the computer. A DC power supply with constant voltage is also attached to the fabric sample to supply the required voltage. For most samples, the voltages are applied for 6 mins and then the voltage is turned off and the temperature decrease is monitored for another 4 mins. In some cases, because the sample fails under the voltage applied, the times differs for how long the voltage is applied and depends solely on when the sample fails. The change in current of the sample is monitored using a multimeter, also connected to a computer for data collection. The three types of experiments done to quantify Joule heating in samples were:

1. Monitor Joule heating on polyester-cotton transfer printed fabric with variable nanowire concentration using a constant supply voltage.
2. Monitor Joule heating on polyester-cotton transfer printed fabric with variable supply voltage with constant nanowire density.
3. Monitor Joule heating on polyester-cotton and cotton fabric samples with constant supply voltage and nanowire density.

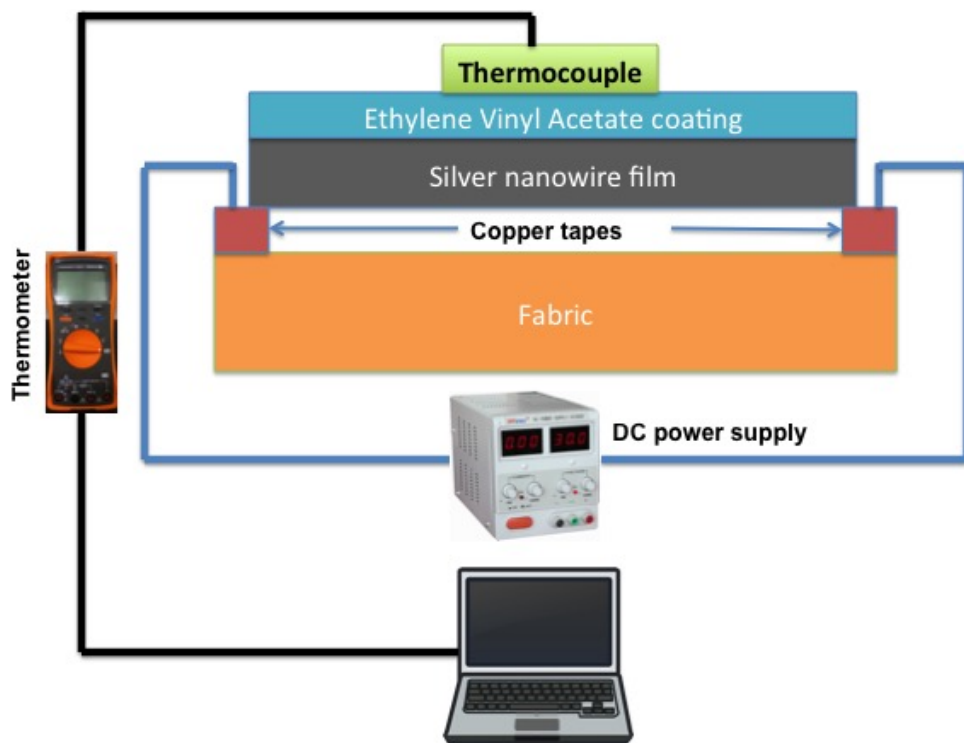


Figure 3.6: Setup for characterizing the Joule heating properties of AgNW fabrics

As seen in Figure 3.7, as the concentration of AgNWs increases, the obtained temperature increases. Since the resistance of higher density NW samples is lower, there is more current flowing through the sample for a given voltage. Since the power dissipated is $P = IV$, these samples create more Joule heating.

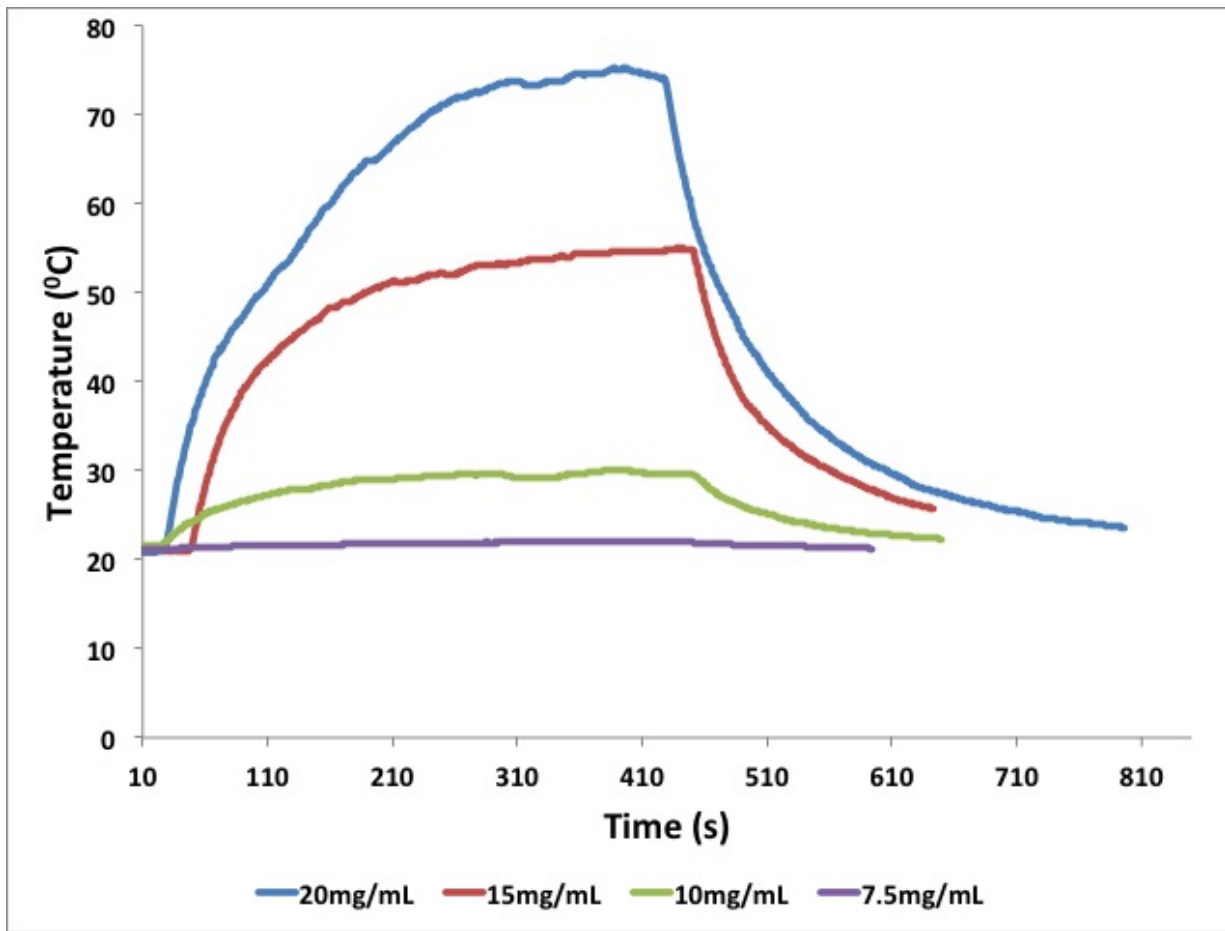


Figure 3.7: Change in temperature for different concentrations of nanowire coatings at a constant voltage of 5 V

Overall, with keeping the voltage at 5 V, it is seen that the temperature can rise as high as 75 °C and 55 °C for 20 mg/mL and 10 mg/mL AgNW coated fabrics, respectively, in under 6 mins. This is a fairly substantial increase and depending on the application the temperature can be tailored using different concentrations of AgNW coatings on fabrics. A dip in temperature is seen when the supply voltage is turned off and the AgNW fabric starts cooling off. It is worth noting that the fabric cools down and returns to room tem-

perature in under 6 mins generally.

As Figure 3.8, where a 10 mg/mL AgNW coated sample is used, shows, with an increase in voltage, the temperature also increases. For AgNW printed fabrics that undergo 1 V and 3 V current, no substantial change in temperature (a rise by 1 °C) is observed. This low change in temperature could potentially be attributed to the fact that the AgNW network does not encounter enough current to exhibit a substantial increase in temperature. But for 5 V and 6 V, 37% (with highest temperature at 30 °C) and 45% (with highest temperature at 33 °C) increase in temperature is observed for the samples. At higher voltages, the temperature change is quite substantial, and shows that amount of temperature change can be controlled both through concentration of AgNWs used and the voltage applied to achieve Joule heating.

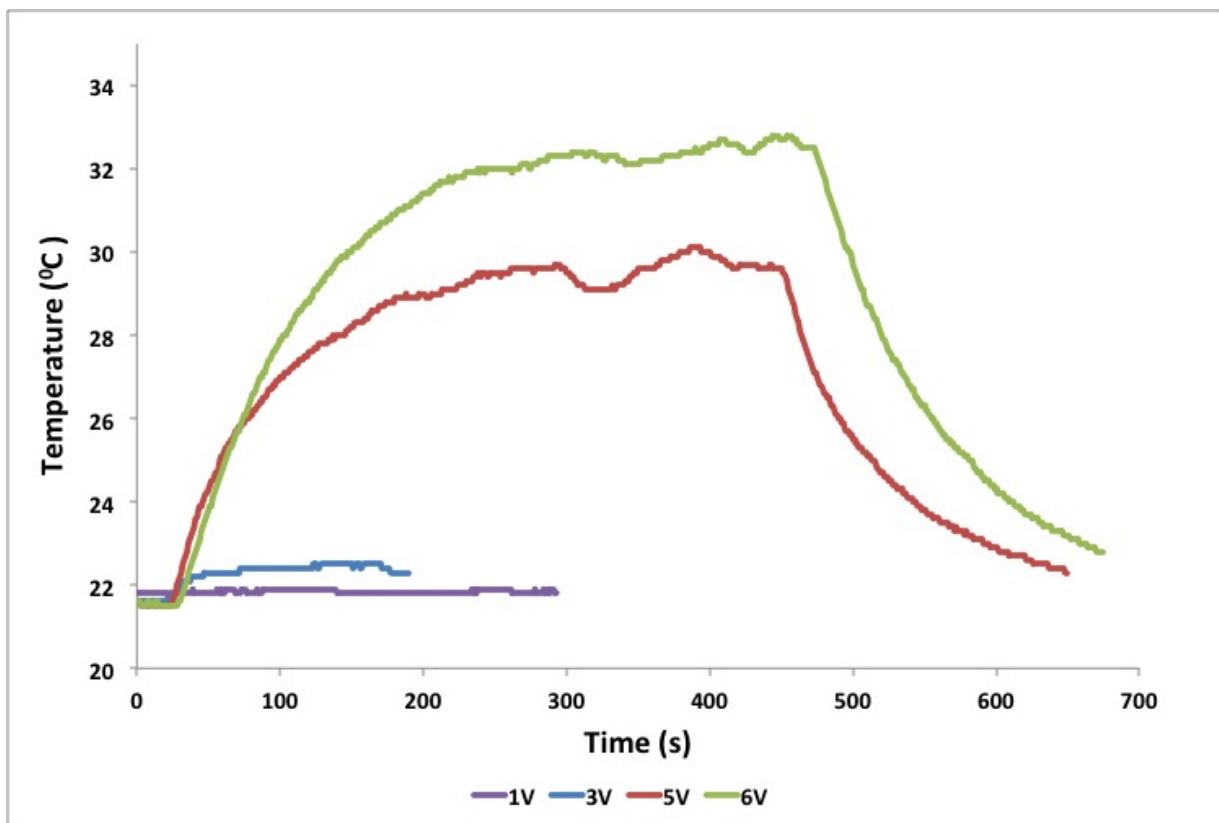


Figure 3.8: Change in Joule heating for various voltages applied across a 10 mg/mL concentration silver nanowire film on polyester cotton.

When a 5V DC voltage is applied to 10, 15 and 20 mg/mL samples, currents of 50, 222 and 480 mA are observed. For voltages over 6V, a breakdown is observed for the samples. The term breakdown refers to the drop in current from the maximum value when a certain voltage is applied to 0 in a matter of few minutes. The Joule heating that occurs evidently leads to a temperature that causes the NWs to melt. Even though the temperature of the coating as a whole is quite low, the temperature of the NWs themselves is much higher [74]. This melting causes a disruption of the AgNW coating on the fabric, thereby reducing the current carrying paths. This increases the current load of the remaining paths, which

in turn increases Joule heating there and leads to their failure as well, until there are no continuous pathways left.

3.5 Conclusion

The option to design and pattern nanowire films onto fabrics opens up endless possibilities. One of the future applications of this method is transfer-printing NW-ink antennas on fabrics using transfer printing. Since with future optimization the AgNW ink may be able to be transparent, this opens up the possibility for seamless device integration. Coleman et al. [75], showed that AgNW inks can be inkjet printed onto PET. Combining this with the process developed and studied in this research, one may be able to print conductive AgNW patterns at home and transfer them onto the clothing and other textiles. AgNW coated fabrics show that there is a direct correlation between shielding effectiveness and conductivity of the AgNW networks. More importantly, one can correlate and achieve different EMI shielding, as per the demand of the applications with the density of AgNWs used. These fabrics can effectively absorb EM waves while being bendable and flexible. The AgNW coated fabrics also show a change in temperature when a current is passed through them. This work only shows a few applications of transfer printed AgNW and can be extended to enable devices like antennas and pressure sensors for future work.

Chapter 4

Stretchable conductive thread

4.1 Introduction

So far in this thesis, there has been a lot of discussion on the use of conductive fabric for enabling electronic textiles. But as mentioned in Chapter 1, conductive threads are also an option to make fabrics conductive. One method to make a conductive thread is to coat their surface with a conductive material such as a conductive polymer, metallic nanoparticles, or carbon nanotubes. The work done by Atwa et al. [76] shows the use of silver nanowires (AgNWs) to coat the surface of cotton, polyester and nylon threads to make them conductive. The AgNW coating has several advantages over other coatings materials used to achieve conductive threads. These include its lighter weight and high mechanical flexibility (i.e. high resilience to change in resistance over multiple bending cycles).

In addition to being bendable, washable and conductive, conductive threads should also ideally have some amount of elastic stretchability. The stretchability of the thread is

important for several applications in e-textiles including strain sensors, clothing, sporting apparel, health monitoring, fencing garments and stretchable batteries. However, there are only a few options of conductive thread that exist in the market. These threads are either made of stainless steel, silver (using plating) or carbon black. One example of a carbon black-based stretchable thread available on the market has an initial resistance of $150 \Omega/\text{cm}$, which firstly, is a very high starting resistance, and secondly, the resistance increases by over 100% in a single stretch [77]. Most of the stretchable conductive threads are made by wrapping a non-stretchable conductive wire around a stretchable thread to make a multifilament conductive thread. These have limited stretchability, high weight and high resistance [77].

In this chapter, a dip coating technique for coating AgNWs on threads, as used in the work done by Atwa et al. [76], is used and the ability to make the conductive thread stretchable is investigated. This chapter outlines the coating strategy for the threads, the different experiments designed to make a successful conductive thread and the hypothesis why AgNW threads retain conductivity over several stretch cycles. Portions of this work were published in the *Journal of Materials Chemistry C* in 2015 [76].

4.2 Experimental methods

To monitor the how and why the resistance of the AgNW-coated thread changes with stretching cycles, two different coating strategies are employed. The first is to coat a stretchable thread with AgNWs in an un-stretched state and then perform stretching cycles for measuring the change in resistance. The second option is to coat the threads in a stretched state, and then test the change in resistance with stretch-relapse cycles. The

thread materials used for the experiment were nylon (monofilament) and polyester rubber (28% polyester and 72% rubber). The threads, are coated with AgNWs in both stretched and un-stretched states. Several parameters are optimized to achieve the ideal coating conditions. These parameters include annealing temperature and time, concentration of AgNWs used, number of coats per thread and the strain applied to the threads. The AgNWs are obtained from Blue Nano Inc. and have 35 nm diameters and 10 μ m lengths. The AgNWs came dispersed in ethanol.

To hold the threads in a stretched state, for both measurement and coating purposes, some specialized equipment needs to be designed, specifically for thread stretch and relapse cycles. In this case, a vice is used (Figure 4.1). The vice is modified by adding metallic grooved patches of metal to either end of the vice side plates. These grooves are about 1 inch deep to hold the threads in position while being stretched. Open semi-circular cylindrical holders were also designed to hold the AgNW solution during the coating process. This allowed for the thread to be fully immersed in the Ag NW solution. This is necessary so that the NWs could coat the full circumference of the thread, rather than just one side (which is what would occur if drop casting was used). The holder was made of stainless steel to avoid any damage by the solvents and by the annealing temperature. Since in one implementation, the threads are coated in the stretched state and need to be annealed in this stretched state, a heat gun was necessary since it wasnt practical to put the whole vice in an oven.

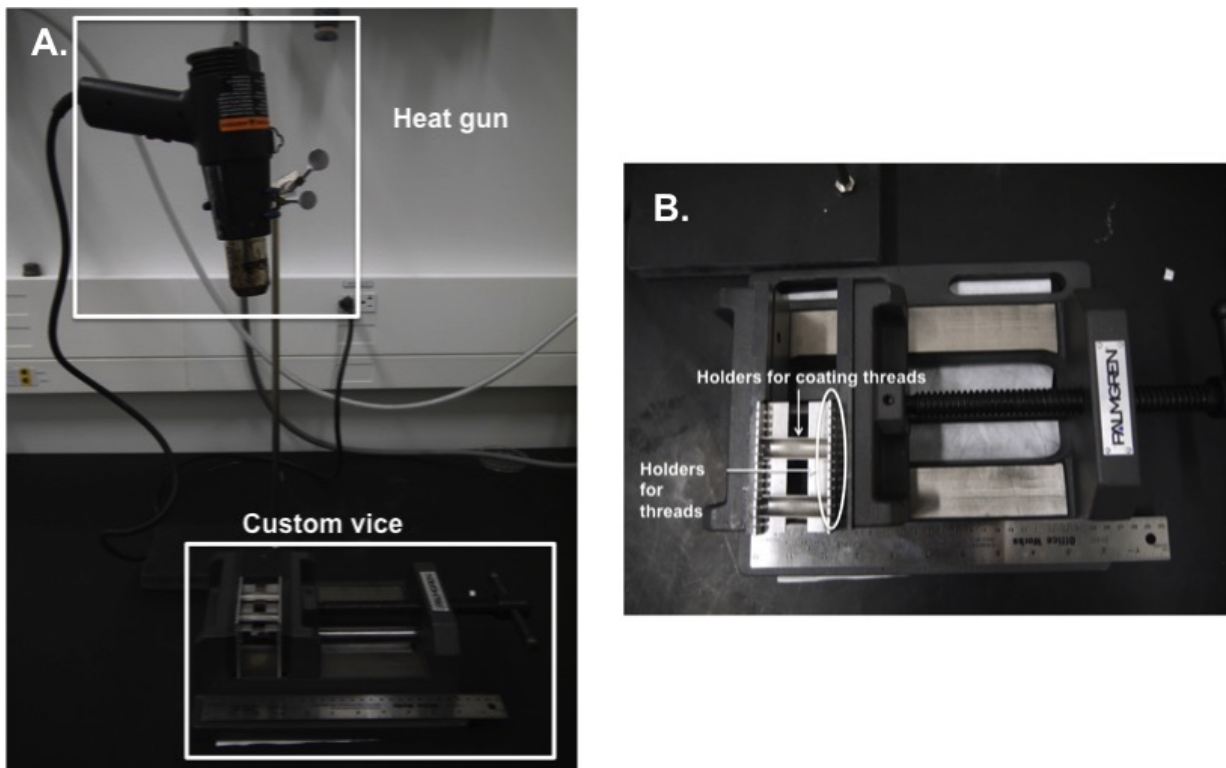


Figure 4.1: Vice setup for coating the threads in a stretched state as well as for stretch-relapse cycle experiments A. Displays the full experimental setup. B. Detailed structure of the vice modification for coating threads

The thread is first cleaned using sonication in a combination of 2 mins in each of ethanol and water. After cleaning, surface modification is done on the thread to improve the adhesion of AgNWs to the threads. The thread is then mounted on the vice, where it is coated with AgNWs by immersing the thread in a AgNW solution (where the solution was held in the specially designed holder described above). The thread is finally annealed in air at 100 °C for 60 mins using the heat gun. The temperature for 100 °C was chosen, despite it being lower than the ideal sintering temperature for AgNW networks, because the threads have a heat tolerance, beyond which melting of the thread happens. For the polyester-

rubber and nylon threads, the heat tolerance is at 100 °C. For measuring the resistance of the thread, copper tape is attached to the ends of the thread and using a multimeter, the resistance of the thread is measured during 10 stretch-relapse cycles. The different AgNW concentrations used for coating are 5, 7.5 and 10 mg/mL. For the second coating technique, the thread is coated in a stretched state of 50% excess stretching compared to its original length.

4.2.1 Thread pre-treatment

Without any surface modification, AgNWs do not stick to the polyester-rubber threads. Heated sodium hydroxide (NaOH) is used to chemically treat the surface of the polyester-rubber thread. The NaOH treatment has a three fold advantage for the threads. First, it helps clean off the impurities that are present on the thread surface. Second, it helps increase adhesion of AgNWs to the thread. Lastly, NaOH helps with the liquid retention capacity of the thread. Polyester is an oleophilic material whereas AgNWs are hydrophilic. NaOH helps hydrolyze the surface of polyester by forming hydrophilic bonds on the polyester chains. This is done by introducing polar groups on the surface of polyester thereby increasing the bonding of the polyester with water molecules [49]. Pre-treatment of textiles with heated NaOH is a standard treatment used in textile industry for scouring of fabrics. Scouring is the process of removing impurities that might be associated with the thread during the processing. For the experiments done here, NaOH is heated to 55 °C and the polyester-rubber thread is submersed in the solution for 6 minutes. After this, the excess NaOH molecules sticking to the thread are not washed off and the thread is directly coated with AgNWs.

The monofilament nylon thread also shows poor adhesion towards AgNWs without any surface modification. Nylon is a synthetic fiber made out of polymeric chains that are hydrophobic. For nylon, a resorcinol modification is used to make the surface of the thread more hydrophilic. The modification entails dipping the thread in a solution composed of 91 wt% ethyl acetate and 9 wt% resorcinol for 1 min. The threads are then dried and coated with AgNWs [76]. The resorcinol modification helps create polar hydroxyl groups on the nylon thread, thereby helping with adhesion of AgNWs to the thread.

4.3 Results and discussion

The monofilament structure of the nylon thread eases the coating process as there is only a single fiber to coat, unlike multifilament threads. The nylon thread is coated in an unstretched state with AgNWs. For a nylon thread coated with this method, an enormous jump in resistance is observed within the first stretch cycle. This happens mainly due to the fact that the AgNWs do not stick very well to the nylon thread. Even after modification with resorcinol, the AgNWs are unable to adhere well to the thread. This causes the AgNW film present on the thread to lift off during stretch cycles and undergo breakdown right away. And since the adhesion is not good for the nylon thread, even coating the thread in a stretched state does not yield good results. Therefore no more experiments are done with nylon thread.

A SEM image of the polyester thread is shown in Figure 4.2. The multi-filaments making up the thread can be seen.

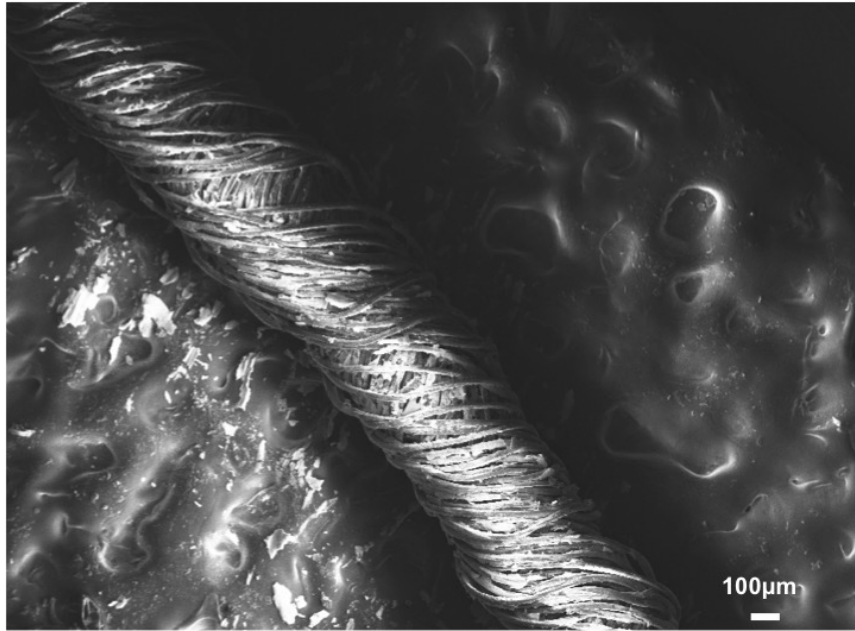


Figure 4.2: SEM image of as-received polyester-rubber thread

The polyester-rubber thread is first coated in an un-stretched state, annealed, then subsequently stretched. After 10 stretch-relapse cycles, the resistance of the thread increased from $9 \Omega/\text{cm}$ to $27 \Omega/\text{cm}$, a 175% increase (Figure 4.3). Set 1 corresponds to stretching the thread from its initial length to a strain of 50%. Set 2 shows the relapse from the maximum length to the original length. For subsequent sets, odd numbered sets are stretching and even numbered sets are relapsing. The increase in resistance after each cycle can be attributed to the fact that contact is lost between some AgNW junctions as the thread is stretched. These once fused junctions cannot reform a low resistance junction when the thread is relapsed to its original length. Thus, less NWs in the coating are involved in conduction and the resistance of the coating increases.

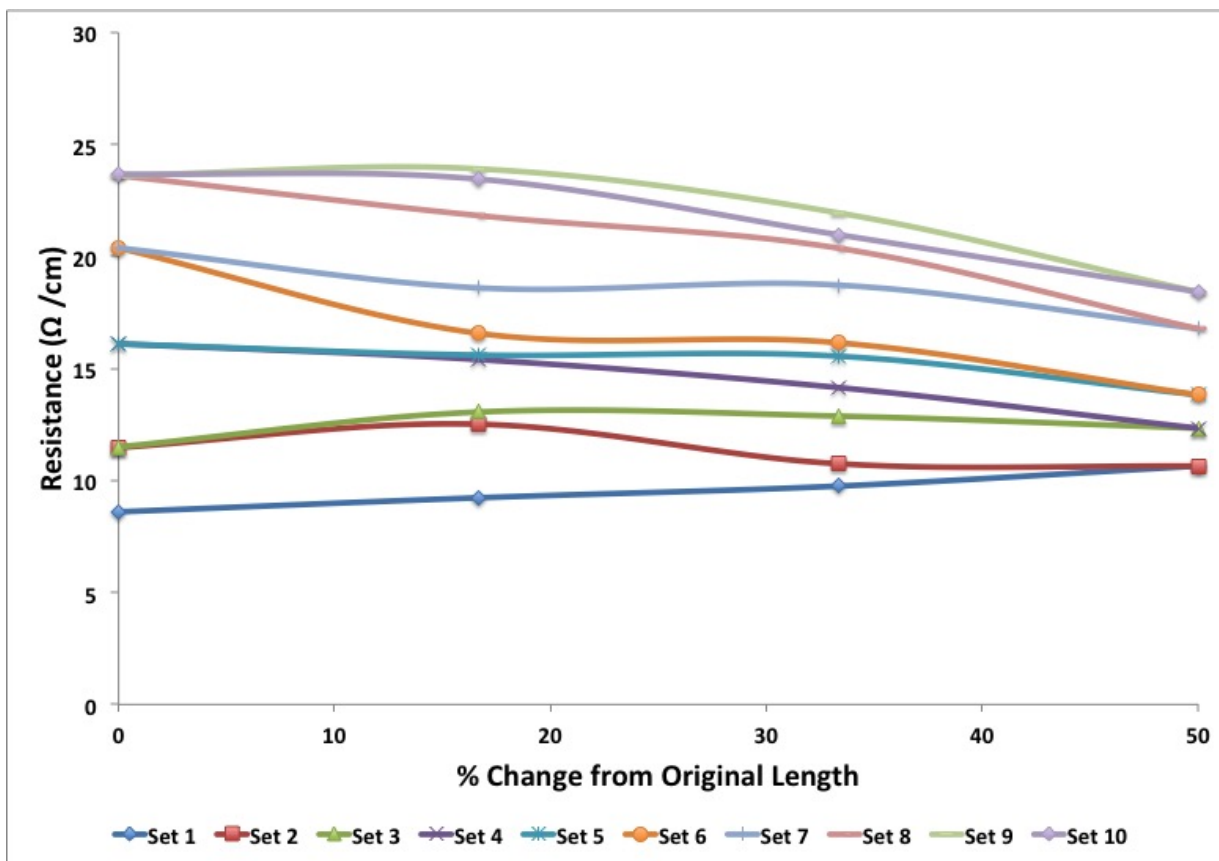


Figure 4.3: Change in resistance of polyester-rubber thread over 4 stretch-relapse cycles when coated with AgNWs in an unstretched state

Because of the poor results when coating the thread in the unstretched state, the second coating strategy is used for coating the polyester-rubber thread, where the threads are coated when strained 50%. The coated threads were then returned to the threads original length, and stretched and relapsed 20 times. Each stretch-relapse cycle took the thread to 150% of its original length (50% strain) and then relapsed back to the original length.

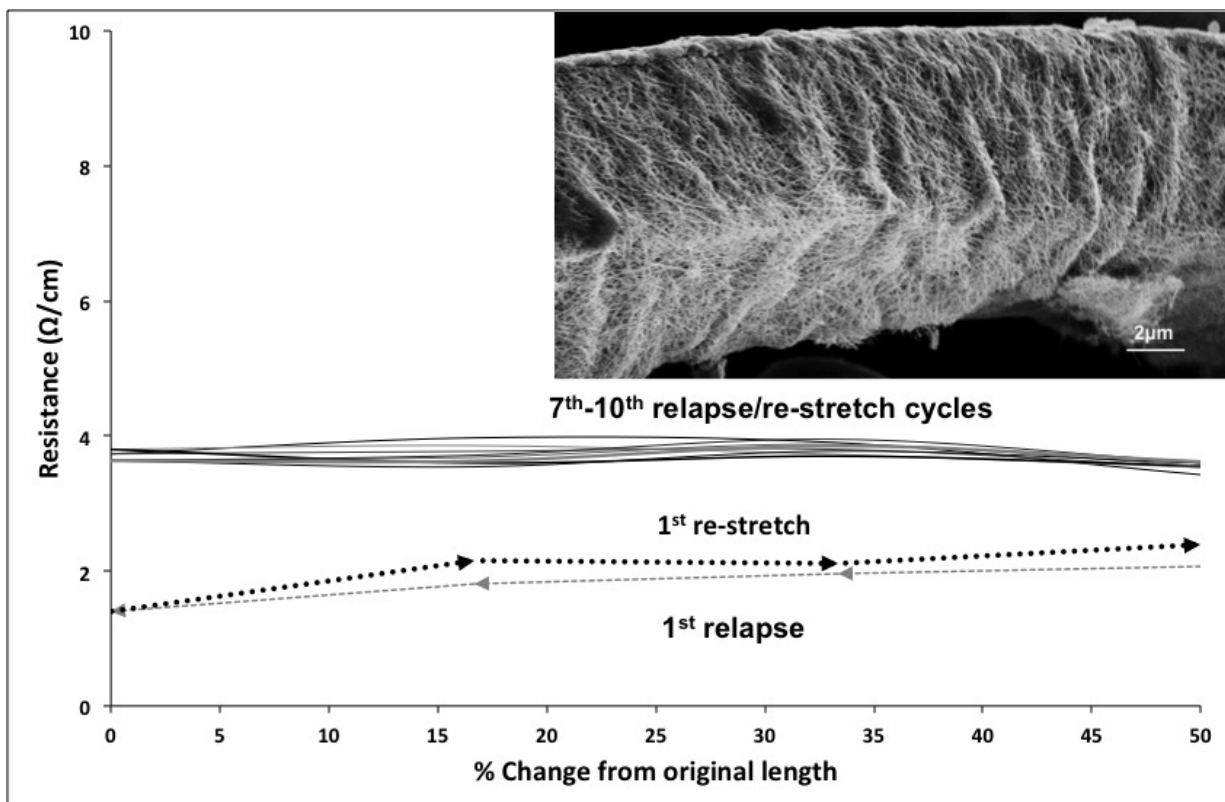


Figure 4.4: Change in resistance of the thread over 10 stretch-relapse cycles. Inset: SEM image demonstrating buckling in the nanowire coating

It is observed that the resistance of the thread initially goes up when stretched then back down when the thread relaxes. This may be attributed to the increased overlapping AgNW of junctions when the length of the thread decreases. The resistance increases from one cycle to the next for the first 6 cycles. Once the 7th cycle is reached, the thread resistance remains relatively constant with subsequent relapse/re-stretch cycles. The inset of Figure 4.4 is an SEM image of one filament of the thread after being stretched 10 times and returned to its original length. A buckling of the nanowire coating can be seen. A flattening out and return to this wavy coating provides a mechanism for stable resistance

with changing strain. A similar buckling strategy has been implemented for stretchable conductive planar thin-films [78].

4.4 Conclusion

Stretchability of a conductive thread is an important problem, both on an industrial scale and research level, considering the myriad of applications it can enable for smart textiles. Threads coated with AgNWs in a stretched state show promise to be able to make stretchable conductive threads, which can retain conductivity of the sample over repeated stretch cycles.

Chapter 5

Conclusion

5.1 Summary and conclusions

This thesis studies the process to coat silver nanowires on fabrics using various coating technologies to achieve conductivity. The work is the first to demonstrate the use of transfer printing to achieve conductive patterns, since standard metal inks cannot be transfer printed. Transfer printing of nanowires is shown to use less metal for a given conductivity, and therefore is significantly lower in cost, than other techniques previously used to apply nanowires to fabrics. This makes the use of metal nanowire coatings much more viable for commercial applications. Transfer printed nanowire coatings was demonstrated on a variety of fabrics, including cotton and polyester, and the coating was shown to be stable with bending and folding.

Overall, transfer printing is a superior technique to print nanowires on fabrics compared to other existing, traditional techniques in the market or research environment. Some of

the advantages of transfer printing include:

1. Ease of application of AgNWs onto fabric.
2. Ease of patterning of AgNWs on the fabric.
3. Allows printing of metallic NWs on various types of natural, synthetic or blended fabrics, whereas dip-coating, brush-coating and drop-casting work well only on natural fabrics [51].
4. Post-textile processing (i.e. does not have to be applied during the textile manufacturing stage).
5. No pre-treatment required for fabric to be coated.
6. No expensive equipment is required like for vacuum deposition or sputtering. If the design can be printed using a printer at home, one could essentially use a hand iron to transfer the metallic pattern onto the fabric.
7. Lastly, it is the most cost effective technique compared to dip coating and brush coating techniques, with the least amount of nanowires being used to coat the fabric to achieve a certain resistance. This is able to produce a low weight, low cost and mechanically flexible coating on the fabric.

As for the use of silver nanowire inks compared to typical nanoparticle and micro-particle metallic inks, the many advantages include:

1. The nanowire fabric provides higher mechanical flexibility compared to nanoparticle inks when printed onto the fabric. Since the nanoparticle inks printed with techniques like screen printing have a high coating thickness, they tend to be stiffer. [79]
2. Although not proven in this thesis, the final product is should be comparatively more stretchable compared to nanoparticle inks, since stretchable and conductive nanowire-plastic composites have been demonstrated by others. [79]

3. Achieving high transparency of the coatings which is not possible with nanoparticle or microparticle inks [35]. With optimization, the nanowire coating could be made even more transparent than what was demonstrated in this work.
4. Comparatively, less amount of metal is used when compared to nanoparticle inks [71] resulting in a lower weight and adding less thickness to the textile.
5. One is able to engineer the conductivity of the textile over a wider range than is possible with nanoparticles. For nanoparticles, the resistances of the conduction fabrics are typically $2 \Omega/\square$ or less [80] [34] [81], since at lower densities a continuous film is not formed. However, with nanowires one can achieve a percolation network at a quite a low density and thus lower conductivity coatings are achievable that use a low amount of metal.
6. Although not proven in this work, the open spaces between the NWs may allow the coating to be breathable, unlike continuous metal inks.

The work on stretchable conductive thread that is discussed in this thesis shows that the thread is able to retain its conductivity after several stretch cycles due to the buckling effect of the AgNW coating. A challenge in industry right now is to produce a conductive fabric or thread that offers high stretchability along with retaining conductivity. Nanowire networks on threads may be an alternative to currently existing options.

5.2 Future work

The transfer printing technique developed can undergo more optimization and enable several more features. Some of the future work in terms of optimizing the technique would involve designing a transparent nanowire coating on fabric while maintaining the conductivity of the sample. One way to maintain the conductivity of the coating while making

it more transparent could involve making an in-lab adhesive layer on the peel-able paper part of the transfer paper, in order to reduce the surface roughness. This would help in producing a flatter AgNW film, with lower resistance of the AgNW film and eventually the use of a lower density of AgNWs, leading to a more transparent film. If an in-lab made polymer can also be annealed at a higher temperature, that would reduce the resistance of the AgNW films since the NWs fuse better at higher temperatures. The future work also involves understanding in-depth the mechanism that causes the increase in resistance when the peel-off of the transfer paper happens. Understanding this phenomenon should also lead to solutions for how to reduce the resistance jump caused by that step.

Another future study would involve encapsulation of these nanowire coatings with epoxy or silicone to improve their lifetimes and increase their washability. Another aspect would be studying and optimizing the printing of nanowires films on stretchable fabrics so that there is minimal resistance change over many stretching cycles.

Some of the applications that these AgNW coated textiles should be analyzed for, beyond what was tested for in this thesis, could include building wearable antennas for clothing that are transparent and flexible, testing their antimicrobial properties and testing their ability to reflect infrared (IR) radiation. For wearable antennas, a lot of research has been done using micro particle and nanoparticle inks to make antennas on fabrics [82], but it has not been done using AgNW coatings, which can provide many benefits as outlined above. Regarding anti-microbial properties, the anti-microbial properties of silver are well known. Silver nanoparticles exist in commercial products such as socks as an anti-microbial treatment, and using silver nanowires instead again would have the benefits listed above. Lastly, the IR reflection of AgNW dip-coated textiles has been shown to reflect body heat

and thus be useful for thermal management in clothing [38]. The IR properties of transfer printed nanowire coatings should be tested since these coatings, unlike the dip-coated fabrics, could both use less nanowires and be much more transparent for their seamless integration into e-textiles.

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