

Parametric Studies of Field-Directed Nanowire Chaining for Transparent Electrodes

by

Jehad Alsaif

B.Sc., University of Hail, 2013

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ABSTRACT

Transparent electrodes (TEs) have become important components of displays, touch screens, and solar photovoltaic (PV) energy conversion devices. As electrodes, they must be electrically conductive while being transparent. Transparent materials are normally poor conductors and materials with high electrical conductivity, such as metals, are typically not transparent. From the few candidate materials, indium tin oxide (ITO) is currently the best available, but indium is an expensive material and ITO cost has risen with increasing demand. Therefore, alternative materials or methods are sought to encourage production needs of applications and help in reducing their price. This thesis presents and discusses results of experimental work for a method, field-directed chaining, to produce a TE device which is nanowire-based, with a figure of merit $\text{FoM} = 2.39 \times 10^{-4} \Omega^{-1}$, comparable to ITO but with potential for far lower cost.

Using electric field-directed chaining, multiple parallel long chains of metal nanowires are assembled on inexpensive transparent materials such as glass by field-directed nanowire chaining, using methods first demonstrated in our laboratory. In this work, we have improved the fraction of functional chains, by tuning the field/voltage, a key step in increasing the FoM and lowering the cost. The effect of operating parameters on TE optical and electrical properties has been studied and identified as well. From experiments with twenty seven substrates, each with a range of electric field and nanowire concentration, the highest light transmission achieved is 78% and the lowest sheet resistance achieved is 100 Ω/sq . Among all the operating parameters, the electric field has the most significant influence on the

fraction of nanowire chains that are functional. In the operating range of electric field strength available to us, we observed a monotonic increase in the fraction of functional nanowire chains. We found a counter-intuitive change in TE properties in a sub-range of nanowire concentration, associated with a change in the structure of chained patterns.

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DEDICATION

To my parents, Ali Alsaif, and Zahawah Alsuwaina,
To my lovely wife, Malak Alsaif,
To my brothers and sisters, Majed, Salem, Baha, Wafa, and Haifa,
and To my beloved son, Ali

Chapter 1

Introduction

Transparent electrodes (TEs), also commonly called Transparent Conductive Electrodes (TCEs), are present in cell phones, displays, solar panels[1], and other devices common in daily life. The wide range of TE applications in entertainment, security, communication, education and most importantly solar energy conversion devices, makes the commercial potential of improvements in cost-effectiveness of TEs very significant. TEs require a combination of high electrical conductivity and high transparency. Typically, metals are the materials with high electrical-conductivity, but metal films of thickness only tens of nanometers (nm) are opaque to visible light. On the other hand, transparent material such as glasses and some polymers are typically insulators (dielectrics). Therefore, materials with a combination of the two properties required to produce a TE, are difficult to find.

Indium tin oxide (ITO), a semiconductor material, described later in this introduction, has the best combination of properties known and is the most widely used [2]. However, its high cost and a few other drawbacks have made the search for ITO-free TE materials a strong research field worldwide. Using our laboratory's established research strength in electric field-directed patterning of nanowires (NWs) from a liquid suspension, we asked whether fine chains of nanowires on inexpensive glass could serve to provide the high electrical conductivity and high transparency required for TE applications. Using these ultrafine NWs, with diameter $\approx 200\text{nm}$ and lengths typically tens of microns, the ratio of covered to open area on the glass substrate can be made small, enabling high transparency. Further, if the connectivity of chains is high and the contact between nanowires is strong, the electrical conductance can be made high (resistance low) with high transparency. This enables a high figure of merit (FoM), usually evaluated as the ratio of the light transmissibility to electrical

resistance (Ω^{-1})[3].

We have synthesized such metal NWs, in our Nanoscale Transport, Mechanics & Materials Laboratory (NTMML); some types may also be purchased from suppliers. We have then used a hybrid method, where the microscale electrodes used for generating the electric fields to direct the NW assembly in the form of chains are made by inexpensive photolithography, allowing coverage of large areas with NW chains at low cost.

Since the TEs have to be conductive and transparent at the same time, we will review the mechanisms of conduction in order to select material and method, and understand how that happens.

1.1 Conduction Mechanism

Materials can be classified, in terms of their electrical conductivity, as conductors, insulators, or semiconductors. In general, metals (e.g., silver, gold and copper) are good conductors, while nonmetals are considered to be insulators, for instance most glass, polymers and ceramics. Nonmetals could also be semiconductors, which means they are partially conductive and could be improved when modified. Electrical conduction occurs when the electron in the valence band, illustrated in Figure 1.1, can move easily to the conduction band without requiring a high energy. However, when the band gap is large, as in the case of insulators, an electron requires a lot of energy to be moved to the conduction band, which makes it impossible for the material to be conductive due to the large band gap. Semiconductors are in between the previous two cases, in which there is a band gap but not as large as insulators. Electrons can move to the conduction band by the thermal energy ($k_B T$) unless otherwise specified. Material conductivity (σ) is identified as the sum of the contribution of the positive and negative charge carriers [4] as follows:

$$\sigma = n_n q_n \mu_n + n_p q_p \mu_p \quad (1.1)$$

where n is the charge density (number of electronic charges/ volume), q is the electron charge ($1.6 \times 10^{-19} \text{C}$), μ is the mobility ($\text{cm}^2/\text{V.s}$) and subscripts n and p are negative and positive, respectively. Semiconductors can be classified into two groups based on their conduction band gap between valence band and conduction band: intrinsic and extrinsic semiconductors [4].

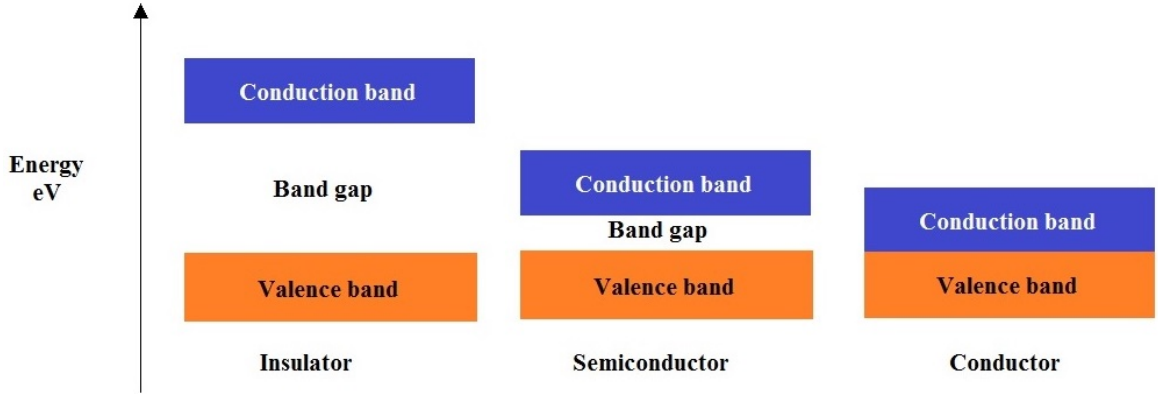


Figure 1.1: Illustration of the amount of energy required for an electron to move to the conduction band from the valence passing the band gap.

1.1.1 Intrinsic Semiconductors

The intrinsic semiconductor material in the periodic table such as in group IV A are tin (Sn), germanium (Ge), and silicon (Si). All of them have a small value of band gap energy (E_g), which is the property of pure material without any addition. In such materials, electrons move to the conduction band by the act of thermal energy ($k_B T$) that gives them a sufficient amount of energy needed to pass the band gap. Hence, intrinsic semiconductors' conductivity increases due to larger number of charge carriers.

When the electron moves from the valence band to conduction band it leaves in the valence band a hole, which is a positive charge carrier. The moved electrons in the conduction band are negative charge carrier. Therefore, conductivity in eq. 1.1 can be rewritten as[4],

$$\sigma = nq(\mu_{electron} + \mu_{hole}) \quad (1.2)$$

since the density of charge carriers in conduction and valence bands, i.e., electrons and holes, are identical [4].

1.1.2 Extrinsic Semiconductor

In this type of semiconductor, impurities, called dopants, have been added to the materials. Doping is the process of adding impurities to the prepared intrinsic semiconductor material. Extrinsic semiconductors are either n-type or p-type. When the dopant material has an excess of electron it is called donor and belongs to n-type

extrinsic semiconductor; therefore, negative charge carrier is dominant. Whereas if it has higher electron holes, i.e., higher positive carrier, it is referred to as p-type. To illustrate, adding phosphorus dopant that has five valence electrons to Si which has four valence electrons in its outer shell affects the energy band since four out of five valence electrons in phosphorus is required to bond. Therefore, an extra electron is left out and acts as a conduction electron in which there is a high negative charge carrier. Hence, phosphorus is n-type dopant. On the other hand, when aluminum, that has three valence electrons, is doped, bonds with Si with a shortage of one electron results in one hole. The hole, as discussed, is a positive charge carrier making Al dopant p-type [4].

1.2 Why are Alternatives to the Leading Material (ITO) Being Sought?

Indium tin oxide (ITO) is the best performing material known for transparent electrode fabrication. With its excellent optical and electrical properties, that reach to 95% light transmission and as low as 10 Ω/sq in sheet resistance, we may ask why there is such a great effort in finding other alternatives to ITO.

One of the main reasons is that indium prices have shown volatility and risen dramatically in the past decades. As shown in Figure 1.2, the price of indium increased to 7 times its value since 2002, reaching US\$750 per kilogram due to the high demand. As seen in Figure 1.3, world indium production has been increasing since the 1980s, reaching 755 ton per year in 2015. This increase is mainly due to ITO fabrication since 90% of indium production goes toward making ITO used for TE applications. Continuing with a total dependency on indium may cause material shortage, resulting in production slowdown. Duan et al.[5] expected that the production in the year 2020 will be around 1100 tons based on the current manufacturing rate, loss rate and production increment rate. Even countries such as China, with approximately one third of world's indium reserve according to US Geological Survey (USGS), would face indium shortage in order to supply the domestic demand [5]. Further, ITO-based TEs are brittle by nature. Hence, it causes a huge limitation in flexible screens and wearable devices [6] and other applications that require flexibility [7].

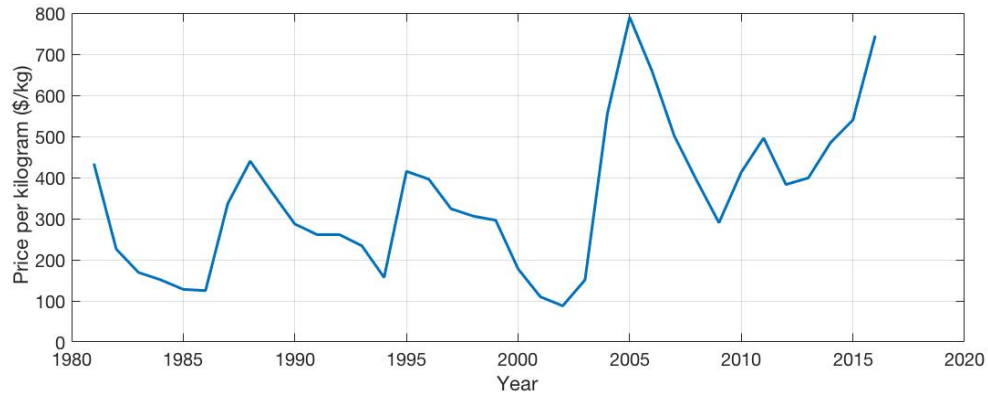


Figure 1.2: The volatility of indium price over 35-year period [8].

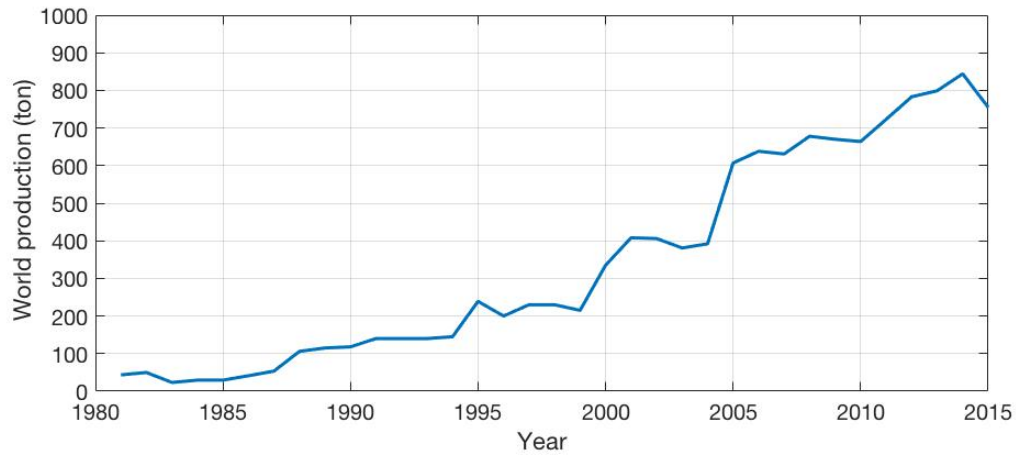


Figure 1.3: Indium production over 35-year period [8], showing that the production of indium is continuously increasing since the 1980s.

Moreover, the most widely used techniques for ITO-based TE production require high vacuum and high temperature, which limits throughput rate and entry of new manufacturers. ITO fabrication and deposition techniques are discussed in Chapter 2.

1.3 Impact of the New Approach

During the MASc research, a new approach for TE applications has been tested that solves many ITO-based TE problems. Our approach is a promising candidate to create a replacement for ITO for several industries and applications. The TEs in this work combine nanowire directed assembly with a convenient microfabrication technique to

pattern the assembly electrodes over large area. This reduces the production cost and makes the assembly process cost independent of the area. Using microfabrication by photolithography, discussed in Section 2.2.7.2, we can produce several substrates at a time. Also, nanowires from a liquid suspension with concentration in the range of 10^8 NWs/mL can be assembled without clumping.

The nanostructure is controlled by the assistance of the electric field, which allows the defining of nanoscale patterns. Therefore, very expensive tools such as Electron Beam Lithography (EBL) or Focused Ion Beam (FIB) are not needed for creating ordered nanoscale patterns in this process. Such tools are useful for single devices, but expensive to operate if a large area coverage is required. In this work, the nanowires are largely aligned in the electric field direction, compared to the random orientation achieved by other deposition methods. We create ordered nanoscale patterns with uniformity in the conductive nanostructure. NWs are forced to connect to each other by dipole-dipole interaction in the direction of the electric field. As a result, we obtain a high electrical conductance, in the range seen for ITO. Other competitive methods, discussed in Chapter 2, have the NWs spread and oriented randomly.

The process of producing such transparent electrodes is simple and performed at room temperature and ambient pressure. With our methodology, it is possible to use different types of nanowire material and to use the substrate repeatedly. This helps in reusing the substrate if the conductive material has degraded. Additionally, this technique allows nanostructure assembly on polymers to produce flexible TEs, which overcomes the brittleness issue that comes with ITO use. In this work, we show the effects of operating parameters on optical and electrical properties. The optoelectronic properties determine the suitability of the TE for the desired application.

1.4 Agenda

In this thesis, work has been done to find an alternative to ITO with comparable efficiency and suitable for applications that require TEs. Many factors could reduce suitability of the presented and examined TE. Therefore, the project involved different stages that include reading, experimenting and evaluating the results. This thesis includes the following:

Chapter 2 describes the available material and methods for producing TE and their advantages and disadvantages. Moreover, the chapter discusses each approach and briefly explains the methodology and the final results.

Chapter 3 illustrates the new and unique methodology for producing TEs, nanostructure control, and disruptors to this technique.

Chapter 4 includes the experimental setup explained in detail, as well as operating parameters used for producing surface nanostructure on a transparent material.

Chapter 5 presents and discusses the results of examining the properties of the final TE. Furthermore, this chapter discusses observations noted during the experiments, including the effects of operating parameters and evaluates the final application.

Chapter 6 provides concluding remarks of this work as well as presents the final statement and contributions of the thesis. The chapter also points to future work in which other interested researchers can pick up from where this work left off. It presents other ways to enhance and develop the efficiency of TEs based on published papers and research.

Chapter 2

Methods and Materials in Use for Transparent Electrode Fabrication

Several factors motivated a major effort, with various approaches, to find alternatives to the leading material (ITO) in the TE industry, as discussed earlier in Chapter 1. TEs must be mass-producible, constraining the materials or methods chosen. Each application requires a certain range of sheet resistance and light transmission. Table 2.1 shows the range of required transparency and sheet resistance for some common applications.

Table 2.1: Current ranges of transparency and sheet resistance sought for the most common applications [1]

Application	Sheet resistance range (Ω/sq)	Transparency range (%)
Solar cells	<20	> 80
Displays (LCD)	<300	> 87
Touch panel	<1500	> 86

This chapter discusses the available approaches and alternatives to the leading material.

2.1 Indium Oxide Film-Based TEs

Indium oxide (IO) has been widely used for commercial transparent electrodes. IO film has a polycrystalline structure with high electron mobility, resulting in low elec-

trical resistivity values (typically $\rho \approx 10^{-3} \Omega\cdot\text{cm}$). Undoped IO has band energy ranging from 3.5 eV to 3.8 eV [9]. However, when doped with an appropriate dopant, such as tin, electrical resistivity decrease by one to two orders of magnitude [9].

To date, indium oxide doped with tin (ITO) is the best performing material used for TE applications, with transparency as high as 95% and electrical sheet resistance in a range as low as 10 to 100 Ω/sq . ITO can be deposited by various methods such as chemical vapor deposition (CVD), sputtering, or evaporation [10]. Optical and electrical properties vary depending on the deposition technique, heat treatment, dopant content, and operating parameters [11]. Table 2.2 represents a comparison between ITO films fabricated by most common methods [12].

Table 2.2: Comparison between different ITO film properties fabricated using several methods with different operating parameter values.

Method	Operating temperature ($^{\circ}\text{C}$)	Transmission (%)	Resistivity $\Omega\cdot\text{cm}$
CVD	350-450	90-95	$1.5\text{-}1.8 \times 10^{-4}$
Evaporation	25-440	82-92	$1.8\text{-}260 \times 10^{-4}$
Sputtering	25-453	70-90	$1.2\text{-}160 \times 10^{-4}$

Each technique has its advantages and disadvantages. For instance, CVD involves the reaction of one or more gaseous reactive species on the substrate [9]. On the other hand, sputtering and evaporation offer higher quality and purity in the properties of the film [12] because CVD is sensitive to contamination [13]. However, these methods are limited to deposition rates [12]. Further discussion on deposition techniques is available in Section 2.2.4 below.

2.2 Alternatives to ITO

Methods that do not exclusively depend on one specific material are attractive for ITO replacement for TE applications. Such methods are stronger potential candidates as they reduce the threat of total dependency on indium as a major material in ITO films. Such methods involve reducing the covered area or thickness of the conductor to allow higher light transmission. In addition, some of these methods resolve the brittleness in TEs, and allow for flexible TE fabrication. Alternatives can be classified into five

different groups: transparent materials, patterned metal films, ultra-thin metal films, conductive polymers, and nano-structured geometry.

The following subsections present and discuss the current available alternatives to ITO and their properties.

2.2.1 Transparent Nanomaterial: Tin Oxide Film-Based

Tin oxide (TO) is a semiconductor that is used, with an appropriate dopant, for TE manufacturing. It serves energy conversion devices and displays because of its electrical and optical properties. Undoped TO has relatively high electrical resistivity, approximately $1 \times 10^{-2} \Omega\text{.cm}$, which is inappropriate for many applications. The band gap energy in undoped-TO films ranges between 3.9 and 4.3 eV, which is higher than IO films [9]. However, electrical conductance can be enhanced by an appropriate dopant [10]. The doping process in semiconductors, in which impurities are introduced from a different material, has shown enhancement of electrical conductivity by two orders of magnitude [9] [14]. Tin oxide doped with p-type or n-type dopant material has a good electrical conductance while maintaining its optical transmittance value. Most TO films are deposited on glass substrates by spray pyrolysis, sputtering, and CVD techniques [15]. Therefore, doping another material with TO such as fluorine (FTO) or antimony (ATO) are options for ITO replacement[16].

2.2.1.1 Fluorine-doped TO

Doping fluorine with tin oxide films ($\text{SnO}_2\text{:F}$) increases the conductivity of the film. In this approach, conductance and transmittance depend on the dopant concentration. For instance, with 4 % fluorine, transmittance is approximately 80 %, with a resistivity of around $8 \times 10^{-4} \Omega\text{.cm}$ [9]. FTO-based transparent electrodes have a sheet resistance ranges from 20 to 450 Ω/sq [17].

Among the approaches used to produce FTO-based TE, CVD is the most widely used. In addition, it is an expensive tool which could limit many industrial sectors from pursuing this technique. Although FTO is cheaper than ITO [15], FTO involves dependency on fluorine, which could also increase its price due to demand and supply, as experienced currently with indium. The process of producing FTO involves high toxicity, which may harm the environment. Moreover, if sputtering was chosen for FTO deposition, the process requires a high temperature with high vacuum, while the deposition rate is relatively low.

2.2.1.2 Antimony-doped TO

Antimony doped tin oxide (ATO) film is another TO-based transparent electrode. Sb-dopant enhances TO electrical conductance which makes its electrical resistivity approximately $5 \times 10^{-3} \Omega \cdot \text{cm}$. It also features high transparency that ranges between 80 and 95%. ATO film with such properties was achieved using the sol-gel method. This method features solution-processibility, which lowers the manufacturing cost and has a high throughput rate [18]. However, such properties strongly depend on dopant content and solution preparation. Moreover, the process requires several steps in order to achieve these properties. The steps include, surface treatment to increase its tension, multiple spin coating, and solvent removal that requires a high temperature up to 285°C . In addition, the process requires thermal annealing to reduce the electrical resistance, whereby the temperature reaches to 600°C [18]. The sheet resistance of ATO-based transparent electrodes ranges from 100 to $1400 \Omega/\text{sq}$, depending on the post-treatment, dopant content, and the thickness [19].

2.2.2 Transparent Nanomaterial: Graphene

A graphene layer is an extracted layer from graphite that is a two-dimensional material of closed packed carbon atoms distributed in a hexagonal shape. Since 2004, graphene has attracted huge attention due to its optical and electrical properties. A single layer of graphene has light transmission values upto 90% [20]. However, its high sheet resistance is a major challenge since it ranges between 200 and $2000 \Omega/\text{sq}$. One extracted graphene layer or flake, has a thickness of 0.34 nm [20].

Incompatibility with mass production and high electrical resistance in graphene layer are the main reasons of limiting it from being used as commercial TE material. One approach for producing highly transparent and relatively low sheet resistance graphene layer requires the use of CVD. Another approach used to create a graphene layer is by the reduction of graphene oxide (GO). GO is obtained by oxidation of graphite powder in the presence of strong oxidant and acids [20]. Graphite mechanical exfoliation is the basic technique for graphene extraction. However, sheet resistance of graphene-based TE is reduced by adding extra layers of graphene to enhance sheet conductance but light transmission dramatically decreases [20] [21]. To the best of our knowledge, no reports have presented a quantitative relation between the light transmission decrease and the number of layers.

Nevertheless, electrical conductance was improved by chemical doping without affecting the transmittance, for instance by using nitric acid (HNO_3) doping [22]. This method for sheet conductance improvement has the drawback of high acidity. Therefore, further effort is needed to improve graphene production for commercial TE applications.

2.2.3 Carbon Nanotubes (CNTs)

Among the available nanomaterials, CNTs are promising candidates due to their mechanical and electrical properties. CNTs were first reported by Iijima in 1991 [23]. CNTs are suspended in certain solutions that feature solution processibility. Solution processibility is an advantage of nanoscale material which allows fast, large-scale, and low cost production [21]. CNTs can be produced by one of the three major methods which are CVD, electric arc discharge that requires high temperature typically above 1700 °C, and laser ablation [20]. Similar to graphene, stacking CNTs would lead to better conductance but would significantly reduce light transmission. CNTs are deposited on transparent materials by spraying, drop-casting, or dip-coating, discussed in Section 2.2.7.7, for TE applications. Unfortunately, CNTs are limited to 2 mg/mL nanotube concentration in organic liquids as suspension media, resulting in limitations for a large area production. Suspension media can become impurities after drying, which dramatically affect the optical and electrical properties of CNTs-based TE [21]. These limitations appear severe, especially for mass production.

2.2.4 Deposition Techniques

There are different techniques to deposit ITO replacement materials. The following sections discuss the most common approaches with their typical operating conditions. Most deposition techniques require vacuum and relatively high temperature. To illustrate the reason for requiring such conditions, first, we need to discuss gas molecule behavior during migration.

In the gas phase, molecules are colliding with each other and with the wall of the container; however, the mean distance traveled without collision of a gas molecule can be found as follows [24]:

$$\lambda = \frac{5 \times 10^{-3}}{P} \quad (2.1)$$

where λ is in centimeters, and P is the pressure in torr. Therefore, reducing the pres-

sure will increase the mean free path resulting in fewer collisions between molecules. Hence, vacuum pressure is an important parameter in most deposition techniques.

Moreover, deposition rate can be quantified using the impingement flux which can be calculated as follows [24]:

$$Flux = \frac{3.513 \times 10^{22} P}{\sqrt{MT}} \quad (2.2)$$

where M is the molecular weight in amu, and T is the temperature in Kelvin. The flux represents the number of molecules striking a surface per unit area and time (molecules/cm².s). Equation 2.2 identifies the role of temperature, since temperature contributes in controlling impingement flux.

2.2.4.1 Evaporation

Vacuum evaporation is one approach used for material deposition. The source, material to be deposited, is vaporized and deposited onto the substrate surface [13]. This technique requires a relatively high vacuum environment (absolute pressure below 10⁻⁴ Torr). In addition, deposition rate under these operating parameters is between 100 and 300 Å/min [9]. Nevertheless, it is hard to obtain a uniform layer using this technique because the transportation of material's molecules is straight along a line of sight from the source. Substrate rotation during evaporation can overcome this issue. In addition, using multiple sources instead of only one results in better uniformity of the deposited material [24].

2.2.4.2 Sputtering

The sputtering technique involves the use of energetic ions that knock out material's molecules from the material source that acts as an electrode. Molecules are deposited on the surface of the substrate, whereby the substrate acts as an opposite electrode. Target (containing the material) and substrate holders each acts as cathode and anode, respectively [12] [24]. Such an approach requires vacuum pressure of 10⁻² Torr in chamber when sputtering metallic sources. In addition, this technique requires a high substrate temperature that reaches 450 °C [9].

2.2.4.3 Chemical Vapor Deposition (CVD)

CVD is a process that involves chemical reaction of one or more gaseous species on the surface of the substrate. It is another approach commonly used for depositing various materials. In addition, the deposition rate in this process can be 1000 Å/min or higher, depending on substrate temperature and gas flow [9]. Unfortunately, this technique involves special handling to prevent environmental pollution due to the chemical reaction that occurs within the process [15]. This can be expensive for large-area coverage.

2.2.5 Ultra-Thin Metal Films

The technology of ultra high vacuum chambers allows the materials to be sputtered with very low thicknesses, orders of few Å. Ultra-thin metal films (UTMFs) are metal films that have thickness of 10 nm or less. At this low thickness, light transmission occurs since the light scattered is low. However, the UTMFs do not have the metal bulk electrical property due to the presence of discrete islands at thicknesses below 10nm. These islands cause discontinuity in charge conduction in the film, increasing the resistivity [25] [26]. Metals, such as chromium (Cr) and nickel (Ni), were used in this approach. They have been deposited at low thickness, typically 2 nm, which results in light transmission as high as 85%. However, the film shows relatively high electrical sheet resistance, approximately 500 Ω/sq. On the other hand, increasing the thickness enhances electrical conductivity but significantly decreases light transmission [27].

2.2.6 Conductive Polymers

Conductive polymers are another promising approach to replace ITO-based TE; they are solution processable. They are also mechanically flexible which resolves ITO brittleness [7]. However, conductive polymers are constrained by their lifetime before the electrical property degradation [28]. Conductive polymers require post-treatment to enhance their electrical conductance, for example using acidic solution or a high temperature [7].

Among conductive polymers poly(3,4-ethylenedioxy-thiophene):poly(styrene sulfonate) (PEDOT:PSS) has received interest as a TE. PEDOT:PSS is a combination of conductive PEDOT and insulating PSS. PSS is required since it acts as a solvent

and a stabilizer for PEDOT. Post-treatment methods, such as adding sulfuric acid, are considered the most effective approach to enhance electrical conductivity. PEDOT:PSS treated with sulfuric acid results in very high electrical conductance that reaches 4000 S/cm [7]. However, this process is very corrosive due to the presence of sulfuric acid, and is hard to control.

The methodology of Zhang et al. [7] shows a light transmission of nearly 95% with a sheet resistance of 250 Ω/sq at 78 nm film thickness. However, when increasing the polymer thickness light transmission and sheet resistance dramatically decrease. For instance, at a thickness of 300 nm, sheet resistance drops to 75 Ω/sq with light transmission of 65%. Na et al.[29] also used a PEDOT:PSS polymer that shows comparable light transmission to ITO.

2.2.7 Metal Nanostructures

We may wonder about the reason for not using a metal microscale geometry instead of nanoscale geometry for TE applications. Having metals which are opaque in microscale structures would block a large portion of visible light. Visible light wavelength typically ranges from just below 400 nm to around 700 nm. Therefore, nanoscale wires, with a size below the diffraction limit, will allow higher transparency.

There are various techniques for creating nanostructured geometry on a transparent substrate for TE. In this section, different methods are discussed. But first, approaches of micro and nanofabrication techniques are discussed.

2.2.7.1 Top-Down and Bottom-Up Fabrication Techniques

Generally, microscale or nanoscale fabrication involve one of two approaches, top-down and bottom-up. Top-down is an approach to create small modified structures from a top level layer or structure. Alternatively, the bottom-up approach is used to build the pattern on the surface of the substrate. The pattern can be built atom-by-atom, cluster-by-cluster, or layer-by-layer [30]. In addition, the assembly of material from a colloidal dispersion, onto a substrate, is considered a bottom-up approach [24].

Hybrid techniques that involve both top-down and bottom-up approaches are also in use. The top-down technique involves patterning the material into the desired nanoscale geometry. On the other hand, the bottom-up approach involves building the pattern on the surface of the substrate, by material deposition and particle assembly.

The top-down process of patterning at nanoscale (below the wavelength of light), typically involves rastering an electron beam to expose and then develop an electron beam resist. Alternately, focused ion beam (FIB) milling with a rastered beam of metal ions can be used for patterning material by ablation. Such processes are prohibitively expensive for patterning of large areas required for TEs, as detailed in Section 2.2.7.3.

2.2.7.2 TE Microfabrication

Photolithography is the approach that is widely used for microfabrication due to its relatively low cost. The process requires a mask that has the shape of the desired pattern; the mask can be used for pattern transfer to an unlimited number of substrates, if projection lithography is used. The process involves exposing a photoresist film to ultraviolet (UV) light. Using a negative photoresist, in which UV radiation strengthens the polymer by cross-linking of main chains, makes the exposed parts less soluble and slower dissolving when soaked in photoresist developer solution while unexposed parts are soluble. On the other hand, positive photoresist involves the breaking of polymer chains by a photochemical reaction during exposure. In this case, exposed areas of the resist become much more soluble, by approximately an order of magnitude, in the developing solutions. Other factors that could affect the accuracy are the lift-off process and mask tolerances that reach $\pm 1\mu\text{m}$ in some cases.

2.2.7.3 TE Nanofabrication

Among top-down nanofabrication methods, Electron Beam Lithography (EBL) is the most accurate technique that involves patterning of an electron-beam resist, followed by selective deposition (additive patterning) or etching (subtractive patterning) of the exposed area of the substrate. The required geometry is directly entered into the EBL software. However, EBL beam rastering time is directly proportional to the area to be etched. Therefore, it may take a considerable amount of time for large areas. Hence, it is not a good choice for large-area nanoscale patterns since it would be very expensive. As an example, industrial rate of EBL is CAD\$60 per hour (based on Simon Fraser University 4D labs user fees, 2017) industrial costs with more stringent controls may be higher. An accuracy of below 10nm can be achieved by EBL [31].

Nevertheless, other techniques have been used for creating nanostructured geometry which are cost-effective and have a high throughput rate, such as electrospinning,

nanowire drop-casting and nanowire spraying. Such methods do not show uniform nanostructure geometry and are characterized by randomness, meaning the details of the structure cannot be controlled in the procedure. As a result, consistent light transmission and sheet resistance values are difficult to obtain. The properties of TEs fabricated by these techniques are further discussed in Sections 2.2.7.5 and 2.2.7.7 below.

2.2.7.4 Patterned Metal Films

Patterned thin metal films result in very high transparency with low electrical sheet resistance. However, the process for such TE properties requires expensive tools such as EBL. Groep et al.[32] produced patterned metal film-based TE. Grid-like nanowires, with widths of 30 to 100 nm, have been fabricated in a square-shaped network. The process results in optical and electrical properties comparable to the properties of ITO. In fact, it is considered to be one of the best ITO replacement. It has been reported that light transmission is as high as 91% with sheet resistance of $50\Omega/\text{sq}$. The TEs, however, were fabricated using EBL technique that patterns glass surface with a given dimension in nanometer scale. As discussed earlier, such a technique is not suitable for industrial sectors due to its cost and incompatibility with mass production [32].

2.2.7.5 Electrospinning

Electrospinning is a process that can be classified as a top-down/bottom-up hybrid technique. Electrospinning process results in nanostructured geometry of a conductive material on a transparent substrate. The process shows capability for TE application. Electrospinning is a multi-step process that involves arbitrary spinning of a fine polymer thread with nanoscale geometry on a conductive layer. The polymer is injected into a syringe pump that has a nanoscale needle hole connected to a potential source. The opposite pole in the voltage source is connected to the substrate (known as collector). The collector has a conductive layer, which is wet etched after spinning, using the spun-polymer fiber as an etch mask. The setup for the process is illustrated in Figure 2.1.

He et al.[33] presents a study that uses the electrospinning technique to produce nanostructured geometry for TE. A layer of chromium (Cr) has been deposited on a transparent substrate. Later, polyacrylonitrile (PAN) fiber was electrospun onto

the deposited metal film surface. After that, the exposed metal parts were etched away where PAN was acting as a protective layer. The process results in high light transmission up to 83% with sheet resistance of $6\Omega/\text{sq}$. The process was repeated with a thinner layer of Cr and resulted in a higher light transmittance(90%) and a higher sheet resistance of $25\Omega/\text{sq}$.

Nanowires produced by electrospinning typically have the advantage of lower sheet resistance when compared to other techniques. The reason is that there is no nanowire-nanowire contact resistance which can dramatically affect the sheet resistance in other methods. Nanowire contact resistance is discussed later in Chapter 5. However, the structure in this process is random and the produced nanowire orientation can not be controlled as seen in Figure 2.2.

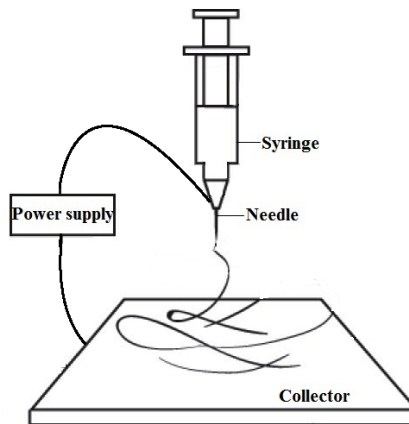


Figure 2.1: An illustration of electrospinning process.

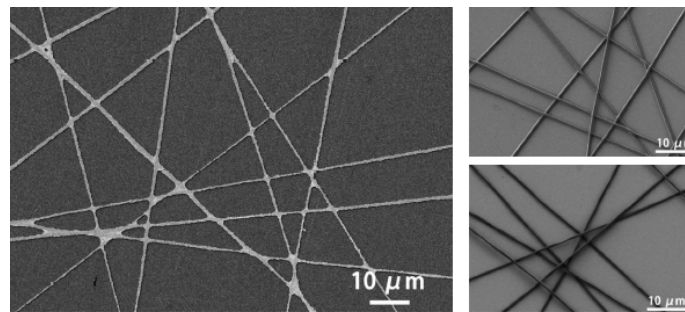


Figure 2.2: SEM images of the nanostructure via electrospinning (He et al. [33]) that shows the randomness of the structure.

2.2.7.6 Nanoimprint Lithography for TE

Nanoimprint lithography (NIL) is a method that also has been tested for ITO replacement. It shows high electrical conductance and transmittance. NIL has a lot in common with photolithography. In fact, both techniques fall under the lithography umbrella. In the NIL process, resist is involved for producing nano geometry; in this case mechanical pressing is used for pattern transfer, instead of EBL exposure. The principle of NIL is applying pressure on a patterned mold that has contact with resist that causes deformation of the resist surface as illustrated in Figure 2.3. Consequently, the deformed parts are etched away faster. Following the etching step, a material is deposited via a selected technique. Nanoscale features on the mold are made by EBL. Using a small-area mold for large area coverage, the advantage is that the mold can be used repeatedly over the surface of the substrate. However, covering large area in this manner poses a challenge with registration of patterns produced by each imprint.

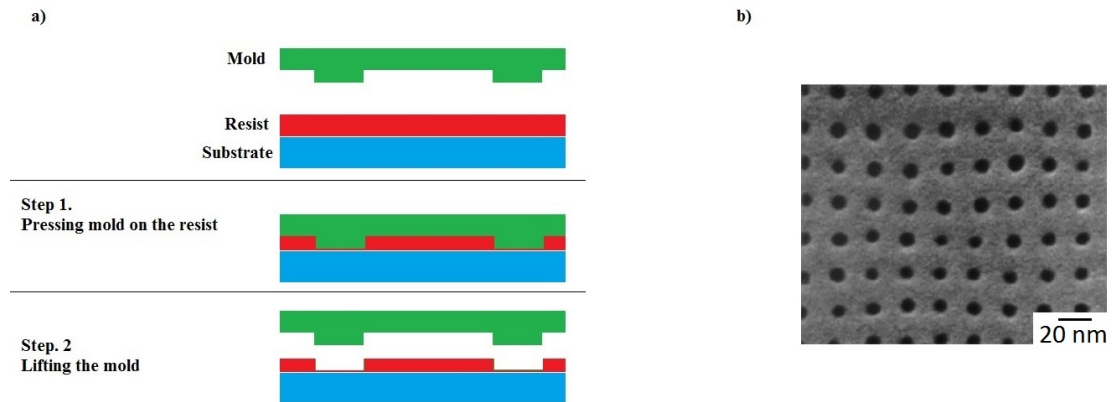


Figure 2.3: a) An illustration of the process and b) SEM image of a hole array with a diameter of 10 nm produced by imprinting technique. Image (b) retrieved from [34].

2.2.7.7 Nanowire Spraying, Drop-casting, and Dip-coating

Other solution processable techniques for nanowire assembly and nanostructured surfaces for TE are spraying[35], drop-casting[36], and dip-coating[37]. These processes feature simplicity and high throughput rate. However, nanostructures on the surface

are random and do not follow a pattern. Therefore, transmission and resistance are not easy to predict.

It has been reported that the spraying method requires a relatively high temperature (110°C) to dry out the NW suspension droplet rapidly. Moreover, the spray flow rate has significant effects on the properties of the substrate. High transparency that reaches 90% and a low sheet resistance of 50 Ω/sq can be achieved by this process [35].

On the other hand, drop-casting involves releasing a few drops of nanowire suspension on the transparent substrate, with the orientation of NWs strongly influenced by the movement of the drying front of the suspended liquid. As a result, controlling the orientation is very difficult and NWs orient randomly [36].

The dip-coating process involves dipping a transparent substrate in a nanowire dispersion, whereby a thin layer of nanowires forms on the surface when it is pulled out of the suspension. The thickness of the nanowire film depends on the number of dipping cycles, pulling velocity, and suspension concentration. A high randomness in the nanowire network is observed in this process as well [37].

Such processes are good candidates in small-sized applications [37] but they suffer from being incompatible with large-sized applications due to non-uniformity in the nanoscale patterns [38]. Also, the connectivity between NWs is hard to obtain with low NW concentrations. Lack of nanowire orientation control is still a major difficulty. To define nanoscale patterns with these techniques, further patterning is required, such as laser ablation or selective etching. These subtractive patterning consume time and results in potential environmental pollution due to the toxicity of NW dust.

2.3 Comparing Alternatives to ITO

As previously discussed, some approaches have optical and electrical properties comparable to ITO, but have other advantages or disadvantages. However, a wide selection of materials and methods would resolve the issue of total dependency on ITO for TE fabrication. Various issues affect ITO and limiting manufacturers from using this leading material. These are material brittleness, indium cost and fabrication tools. Such factors may also limit further improvement in the technology of wearable devices that require flexible displays. Table 2.3 in this section summarizes the range of optical and electrical properties for each alternative, including advantages and disadvantages.

Table 2.3: Comparison between current alternatives

Technique	T(%) range	R_s (Ω/sq) range	Advantages	Disadvantages
Ultra-thin films [27] & [39]	60-85	10 -10K	- Control deposition rate - Wide selection of conductive materials	- Requires expensive tools - Incompatible with high throughput - Requires post treatment - T & R_s depends on metal thickness
Conductive polymers [7]	60-95	25- 250	- Solution processable - Flexible	- Some polymers have high toxicity - High acidity - Post treatment required - Has a lifetime
Electrospinning [33]	83-92	<10 -30	- High conductance - Simple	- Random structure - Lack of nanowire control - Multi-steps process
Graphene [20]	<90	200 - 1000s	- Highly transparent for single layer	- Requires multi-layer for lower R_s - Low throughput rate
Patterned metal films [32]	87-90	30-60	- High transparency and conductance - Shape control - Lack of randomness	- Requires EBL - Cost scale with area - Incompatible with mass-production
CNTs [20]	70-90	60-870	- Solution processable - Quick processes to produce TE films such as spray-coating	- Requires multi-layers for low R_s - Limited concentration when wet deposited
Nanoimprinting [40]	60-90	30-230	- High throughput rate	- Properties depend on material, deposition method and geometry

Depending on the final application and its requirements, the best approach can be determined from Table 2.3. Although many alternatives have reached, or even exceeded, the opto-electronic properties of ITO, several limitations remain.

2.4 Concluding Remarks

The drawbacks of ITO have motivated the search for new methods and materials to produce ITO-free TEs. Alternatives to the leading material (ITO) have been discussed, showing that there are a few challenges in each approach. Tin-oxide film-based TEs have been reported to have excellent optical properties; however, TO has a high electrical resistance. In addition, TO is brittle, which is a drawback shared with ITO. Moreover, TO-based TEs require additional treatment, such as heat treatment to improve the electrical conductivity. Graphene has excellent light transmission. However, the major challenges with it are its very high sheet resistance that reaches 2000 Ω/sq and it is incompatible with mass-production. Similarly, CNTs have a high sheet resistance and are incompatible with mass-production, although high light transmission has been reported. UTMFs feature high light transmission; however, for thickness below 10 nm the electrical conductance is poor. Increasing the thickness of metal films enhances the conductance, but, the light transmission dramatically decreases. ITO, TO, graphene, CNTs, and UTMFs-based TEs require the use of one of the following techniques that have disadvantages including high cost. CVD over large areas requires special handling to prevent air pollution which makes the process difficult and sensitive to contamination. Sputtering and evaporation require special conditions such as high vacuum and temperature.

Conductive polymers have been used to solve brittleness associated with ITO and its alternatives. However, they are limited to a lifetime depending on the surrounding temperature and pressure. Other simple approaches to create a TE include creating conductive nanostructures on transparent material, such as glass. Using EBL, for example, results in very high transparency and low sheet resistance, but this approach cannot be used for industry since it is very expensive. The electrospinning approach that is a multi-step process has been used for TE applications and shows good optical and electrical properties. However, electrospinning, NW drop-casting, NW dip-coating, and NW spraying approaches have random conductive structure whereby repeatability of light transmission and sheet resistance may be hard to obtain. Moreover, in NW drop-casting, dip-coating, and spraying, connectivity between NWs cannot be assured since the NWs are randomly oriented. We next examine the potential of nanowire-chaining based TEs to address these difficulties.

Chapter 3

Nanowire Chaining-Based Transparent Electrodes

Among methods discussed in Chapter 2, photolithography production cost for micron-scale patterns is low, since it does not scale with area covered. In our approach, we first produced substrates with micron-scale electrodes, to create the electric field for assembling nanowires into conductive chains. Nanowire suspension is introduced on the surface of the substrate, while the electric field is applied. Nanowires are polarized by the applied field and pulled towards regions with high electric field gradient due to the dielectrophoretic force acting on the nanowire. Such assembly and nanowire control is classified as a directed-assembly technique, which is one of several available techniques discussed in section 3.1.

3.1 Nanoparticle and Nanowire Assembly Techniques

Nanostructured surfaces are not only used for transparent electrodes but also for nanoelectromechanical systems (NEMS) application, such as mass sensors [41]. When relying on expensive tools, such as EBL, to create such structures, applications will not be commercially viable due to their high cost. Therefore, other methodologies are being used to create structures and assemble nanostructures on a substrate.

3.1.1 Self-Assembly

Self-assembly is a process where particles assemble spontaneously, without externally controlled application of forces or fields, to form larger units. The process occurs under the influence of forces such as electrostatic attraction or repulsion, vander Waals interactions, or fluid forces. These forces arrange particles into particular assembled shapes, because of their interaction with each other, with a fluid medium or the substrate [24]. As an example, formation of layers by self-assembly can occur when an appropriate substrate is immersed into a solution that has an active surfactant.

3.1.2 Nanowire Directed Assembly

By way of contrast to self-assembly, directed assembly requires the use of external forces to manipulate and direct particles towards desired positions. There are several techniques that could be classified as directed assembly, scanning tunneling microscope (STM), for instance. STM involves the use of the tip within the tool to manipulate the particles and direct them. However, this process, as previously discussed, results in unacceptably high cost for large area patterning with particles such as NWs.

A non-uniform electric field causes dielectrophoretic force on polarizable particles. This force can be controlled to cause particles to be carried towards regions of high electric field gradient. This approach is also classified as a directed assembly process which is the core of this work. Further details and discussion are in the following sections.

3.2 Electric Field-Assisted Directed Assembly

When an AC voltage is applied to a suspension of particles, the particles become electric dipoles, with electrohydrodynamic (EHD) forces acting on them. Such forces occur because of the non-uniform electric field. EHD forces include dielectrophoretic (DEP) force, which is a force exerted on polarizable particles [42], in a non-uniform electric field. Using EHD forces, which include DEP force as well as dipole-dipole interaction, we form chains of nanowires between microelectrodes separated by microscale gaps, as illustrated in Figure 3.1. In the following subsections, DEP force involved in NW-chaining is discussed.

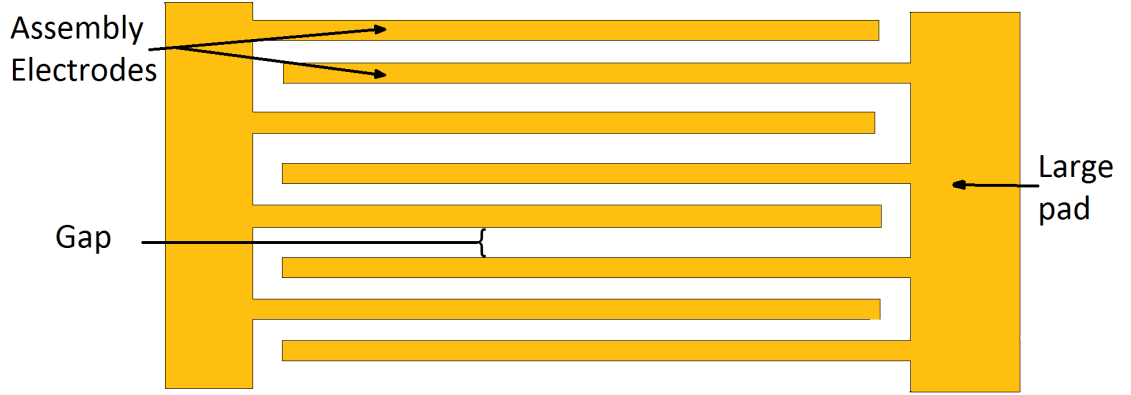


Figure 3.1: Interdigitated electrodes improve utilization of available area for coverage by NW chains.

3.2.1 Dielectrophoretic (DEP) Force

Dielectrophoresis was adopted by Pohl in 1951 [43] to describe the motion caused by the polarization of the particle within the applied non-uniform-electric field as a result of partial charge separation. There are two types of DEP forces. These types determine the direction of the movement of the particle which mainly depends on the polarizability of particles and the medium. The first type of DEP force is negative DEP (nDEP). nDEP occurs when the medium polarizability is higher than the suspended particles, causing the particle to move away from the region of the high electric field gradient. The second type of DEP force is positive DEP (pDEP). pDEP occurs when polarizability of particles is higher than the medium. Here, particles are driven towards the region of higher electric field gradient [44]. In this work, pDEP has been used as the main nanowire assembly director, whereas nDEP is considered to be a major disruptor.

DEP force on cylindrical particles can be calculated as follows [45]:

$$F_{DEP} = \frac{\pi r^2 l}{6} \epsilon_m \text{Re}[F_{CM}] \cdot \nabla (E^2) \quad (3.1)$$

where r and l are the radius and length of the nanowire, respectively. ϵ_m is the permittivity of the medium, E is the electric field, and $\text{Re}[F_{CM}]$ is the real part of

F_{CM} , Clausius-Mossotti factor, that is defined as [45]:

$$F_{CM} = \frac{\epsilon_p^* - \epsilon_m^*}{\epsilon_m^*} \quad (3.2)$$

where $\epsilon^* = \epsilon - j(\sigma/\omega)$, σ is the electrical conductivity, and ω is the angular frequency that equals $(2\pi f)$.

From equations 3.1 and 3.2, it is clearly seen that the magnitude of DEP force is strongly dependent on the electric field gradient and frequency. When the applied potential is 5 V, separated by gap sizes ranging between 120 to 240 μm , the electric field gradient creates a DEP force high enough to pull nanowires towards the electrode edges. In addition, this force has been used for other purposes, such as separation of various types of particles depending on their dielectric properties [42].

3.3 Nanowire Chaining Phenomenon

A droplet of nanowire suspension is introduced onto the substrate (illustrated in Figure 3.1) while an AC potential is applied between micro electrodes. Chains of nanowires are created between assembly electrodes with the following steps (illustrated in Figure 3.2):

1. Some nanowires are drawn towards the assembly electrodes where high electric field gradient exists, (due to positive DEP force).
2. One end of the nanowire with opposite polarity to the assembly electrode is attracted towards that electrode. The other end acts as a new assembly electrode.
3. Dipole-dipole interaction between NWs results in NW chains between the assembly electrodes.

Nanowire chaining occurs when the gap size between assembly electrodes is much larger than the length of the NW. Average nanowire length used in this work is 13 μm , whereas the gap between assembly electrodes is at least ten times longer than the nanowire length.

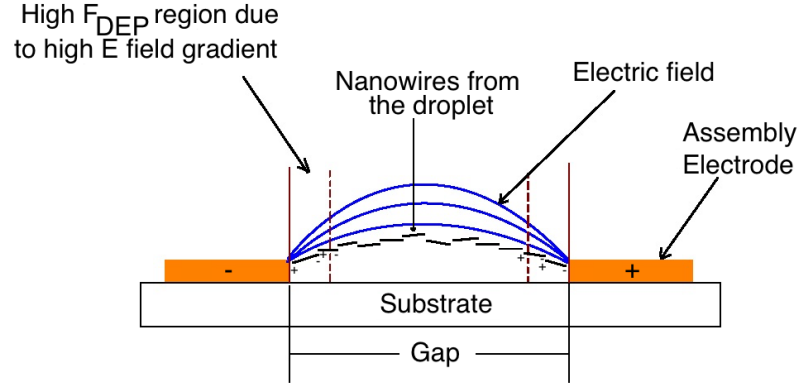


Figure 3.2: Cross-sectional view illustration of electric field gradient and high DEP force region.

3.4 Parameters for NW Chaining Control

To create chains of nanowires between assembly electrodes, several parameters have to be considered as they play an important role in this technique which are:

- Nanowire suspension concentration;
- Electric field strength between assembly electrodes that depends on the applied voltage and gap size;
- Frequency of the applied electric field.

From equation 3.1, it is obvious that electric field strength and frequency have a strong effect on the main directing force (DEP force).

3.5 NW Chaining Disruptors

Choosing improper parameters can allow or create other physical processes which disrupt NW chaining. For instance, low NW concentration leads to insufficient number of NWs to create chains. Another disruptor is the selection of improper frequency that increases the effect of electrical double layer, discussed below.

3.5.1 Electrical Double Layer (EDL)

Since the process deals with metal nanowires (NWs) that are polarizable, understanding the behavior of the EDL is required to illustrate its effects and advantages. The

surface of a conductor with a net charge in an electrolyte attracts a layer of oppositely charged ions, as seen in Figure 3.3. Therefore, fluid adjacent to the charged surface carries the opposite charge to create a balanced charge state around the NW, making the combination of the surface and solution neutral. The surface charge region is often called the Stern layer, whereas the region around the Stern layer where the ions move freely in is called the Diffusive layer, or Slipping plane, as shown in Figure 3.3. The two combined layers make up the electrical double layer (EDL)[46]. EDL length

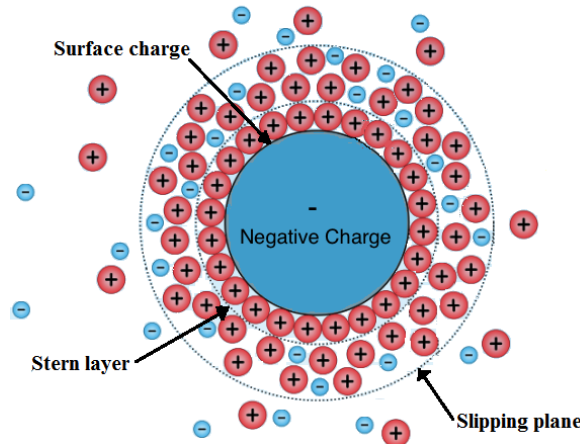


Figure 3.3: Electrical double layer around immersed particle in an electrolyte.

can be expressed using the reciprocal of Debye length as follows [46]:

$$\kappa^{-1} = \sqrt{\frac{\epsilon\epsilon_0 k_B T}{\sum_i e^2 z_i^2 n_i}} \quad (3.3)$$

where ϵ and ϵ_0 are the dielectric constant of the solution and the permittivity of free space, respectively. k_B is the Boltzmann constant, which is $1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$, T is the temperature in Kelvins, e is the electron charge $= 1.6 \times 10^{-19} \text{ C}$, z is the valence of i th order ionic species, and n is the ionic concentration in the solution. As shown in equation 3.3, EDL thickness depends on the dielectric constant of the suspension.

The EDL plays an important role in the repulsive force between two surfaces, due to similar-charges in the EDL clouds. When an EDL is present above assembly electrodes, it acts as a capacitance. Hence, it reduces the effective voltage, which reduces the DEP force. Therefore, we use an AC electric field with a frequency lower than the relaxation frequency of ions and polar molecules in the suspension

[45]. Thick EDL increases the effects of other disruptors such as electroosmotic flow, discussed in section 3.5.2 below.

3.5.2 The Effects of Electroosmotic Flow

Another electrohydrodynamic force is the electroosmotic force, which causes electroosmotic flow. The flow occurs due to the interaction of the applied electric field and free charges in the EDL [47]. Electroosmotic (EO) flow causes a significant disruption if the velocity of the flow is high. In this case, drag force caused by suspension movement may prevent the generation of NW chains. As illustrated in Figure 3.4, the EO flow is vortical and can drag NWs away from the assembly electrode. Therefore, EO flow has to be minimized by reducing EDL thickness, κ^{-1} , above the assembly electrodes.

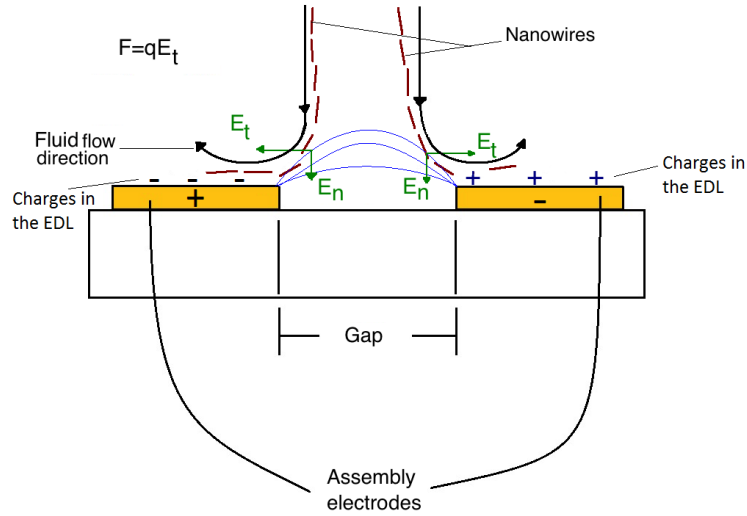


Figure 3.4: Fluid motion between two microelectrodes. Fluid flow is vortical which is caused by the electroosmotic force ($F=qE_t$) where q is the charge in the EDL and E_t is the tangential electric field. Illustration inspired by [48].

EO flow velocity can be calculated as follows^[49]

$$v = \frac{\epsilon_m V_{rms}^2}{4x\eta} \frac{\gamma^2}{(1 + \gamma^2)^2} = \frac{\epsilon_m V_{rms}^2}{4x\eta} f(\gamma) \quad (3.4)$$

where V_{rms} is the applied voltage, x is half of gap size, η is the viscosity of the electrolyte, and γ is a dimensionless function of frequency that is defined as follows:

$$\gamma = \frac{\pi}{2} x \kappa \omega \left(\frac{\epsilon_m}{\sigma_m} \right) \quad (3.5)$$

where κ is the reciprocal of Debye length in equation 3.3. Therefore, EDL thickness plays an important role in EO flow velocity which changes by tuning the applied frequency. Hence, the frequency of the electric field is an important parameter that contributes to the NW chaining process. Sam et al. [45], have defined a range of frequencies that minimize this disruptor. From the framework for NW chaining of NW with similar length, diameter and medium, it was found that 10kHz is an appropriate applied frequency to minimize the effects of EO flow [45].

3.5.3 Capillary Forces from Nanowire Suspension

NWs are suspended in ethanol that has a rapid evaporation rate [50]. In addition, alcohol spreads over the substrate when a droplet is discharged. Due to the surface tension, the suspension may be driven to undesired places on the substrate. Therefore, control over the suspension is required to direct it towards desired places on the substrate and increase the time before alcohol dries out.

To have such control over these aspects, a nanowire chaining dam [51], with wells as illustrated in Figure 3.5, was introduced. Using the wells, of 1 mm width and ≈ 12 mm length, we have significantly improved control over NW suspension spreading and rapid dryout.

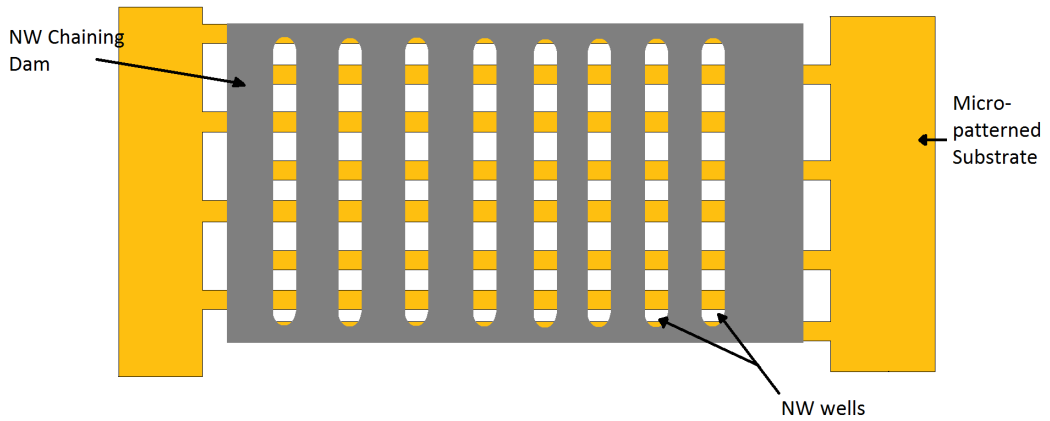


Figure 3.5: Illustration of the nanowire chaining dam placed on the micro-patterned substrate.

Increasing the time before alcohol dries out is the key for creating multiple NW chains; the mechanism is discussed in section 5.4. However, once alcohol starts to dry out, capillary forces may destroy NW chains. Therefore, curvature of NW chains in the direction of the drying front may be noticed if the electric field strength is low, as will be later seen in Chapter 5.

3.6 NW-Chained Transparent Electrode

Mahshid Sam, during earlier doctoral work in our group, introduced the process and introduced a framework for field directed assembly [45][51]. Sam et al. [51] presents a study of various disruptors arising from improperly applied frequency and voltage. However, nanowire suspension concentration and electric field effects on TEs have not been discussed due to the limitation in measurement tools.

Sam et al. [51] present the optical property of substrates with varying assembly electrode gap sizes with chained rhodium nanowires. Substrates result in a light transmission of 65%, 72%, and 69% for electrode gap sizes of 120, 180, and 240 μm , respectively[51]. However, the effects of varying nanowire concentration on light transmission and the sheet resistance of nanowire chains had not yet been studied.

In this thesis, the NW chaining process was carried out towards the making of TEs. In addition, this work investigates NW chaining parameters and their effects on the opto-electronic properties of the substrates. As a result, a comparison can be made between available ITO alternatives from the experimental data. A scope for further research to enhance NW-chain-based TEs has been identified.

3.7 Concluding Remarks

Since the photolithography technique involves low cost for microfabrication over large areas, it has been used to produce micropatterns to create conductive nanostructures by generating NW chains. NW chains are created in micron-sized gaps by applying a nonuniform electric field. The director force to initiate chains of NWs is the positive dielectrophoretic force that acts on suspended particles close to the electrode edges, where a high electric field gradient exists. For low electric field gradient regions in the micron-scale gap, dipole-dipole interaction between NWs occurs, creating a chain of NWs.

The NW chaining process depends on NW concentration, electric field strength, and frequency. The process may be disrupted when selecting improper frequency which allows EDL to form above assembly electrodes; this acts as a capacitance and decreases the effective voltage. In addition, EDL increases EO flow which prevents the creation of NW chains. Capillary force due to the drying front may disrupt the process as well; however, using the NW chaining dam, we minimized this effect. Using the NW chaining dam, we create multiple NW chains across gap sizes of several hundred microns. Our approach ensures the connectivity between NWs. This is enabled by less randomness in the conductive structure as the NWs orient in the electric field direction.

Chapter 4

Experimental Methods for Assembly and Evaluation of Transparent Electrodes

In this chapter, we will discuss details of the methods and explanations of experiments carried out to produce NW-chaining based TE devices. In addition, the experimental set-up for the measurements of electrical and optical properties is discussed. The experiments include nanowire synthesis, chaining parameters, substrate fabrication, as well as measurement of the light transmission and the sheet resistance of the device.

4.1 Nanowire Synthesis

There are numerous available approaches to synthesize nanowires. As discussed in Chapter 2, there is a way to produce nanoscale patterns on a substrate by the electrospinning process, but with little control over the connectivity. A technique used to grow separable semiconductor NWs is the Vapor Liquid Solid (VLS) process. Semiconductor NWs fabricated by the VLS technique have shown a high sensitivity in mass detection and have been used for fabricating nanoscale sensors [52]. The diameter of silicon wires grown by the VLS technique can be controllably varied from 50 nm to 10 μm [53], which is a major advantage of the process. Gold particles are created on a silicon substrate in the form of discrete islands. The substrate is then heated to form Au-Si alloy droplets. A silicon source such as silane (SiH_4) gas dissociates at the droplet surface, with Si atoms entering the surface. A concentration gradient

drives them to the Au-Si interface, where the Si atoms precipitate at the liquid-solid interface. Si layers grow epitaxially [54] and raise the level of the liquid droplet, while adding to the length of the nanowire. Laser ablation of silicon can provide an alternative source of Si-vapor. The VLS process is very efficient and the most commonly used for synthesizing SiNWs.

Another approach, used to grow metal NWs is thermal evaporation of source materials, and is termed the vapor-solid method. The process involves vacuum condition and temperature change, which are the main parameters in this process. The bulk material is heated to reach the vapor state, while an inert gas carries the vapor towards the substrate. In the substrate chamber, the temperature is much lower than the evaporation step, which causes the vapor to solidify on pre-patterned seed regions on the substrate [54]. Further details on creating semiconductor NWs are available in [54] and [55].

The VLS technique is the best way to grow high crystallinity semiconductor NWs, whereas solution-based NW growth is preferable and a very promising technique to synthesize metal NWs. The latter technique can be operated at room temperature and ambient pressure. In addition, it features simplicity, high throughput, as well as a wide selection of NW materials [56]. There are two methods of solution-based NW synthesis: soft template and hard template. In the soft template method, the growth of NW occurs by a chemical reaction where the metal ions are deposited on energetically favorable sites. On the other hand, the NWs in the hard template method are grown inside nanoporous templates [57].

In our lab we synthesize nanowires by a hard-template method, using electrochemical deposition. Electrochemical deposition involves metal ion reduction to fill the pores within a nanoporous template made of anodized aluminum oxide (AAO) or polycarbonate. Commercially available AAO templates are made for filtration; however, we use them as molds to grow the material inside the nanoholes. An AAO template has a nanopore density of $\approx 10^{11}$ pores/cm², with nano-pore diameter of around 200 nm, it yields good cylindrical-shaped wires [57].

The electrochemical deposition process involves a metal ion reduction within the AAO template pores. The process occurs by applying a voltage from an external power supply to provide the required number of electrons to reduce metal ions. The power supply maintains the cathode at a negative potential with respect to the anode. The electrolyte completes the electrical circuit. The cathode is the working electrode where the reduction process occurs. The electrolyte contains desired metal ions which

are reduced. Figure 4.1 illustrates the electrochemical deposition technique used in this work to synthesize NWs.

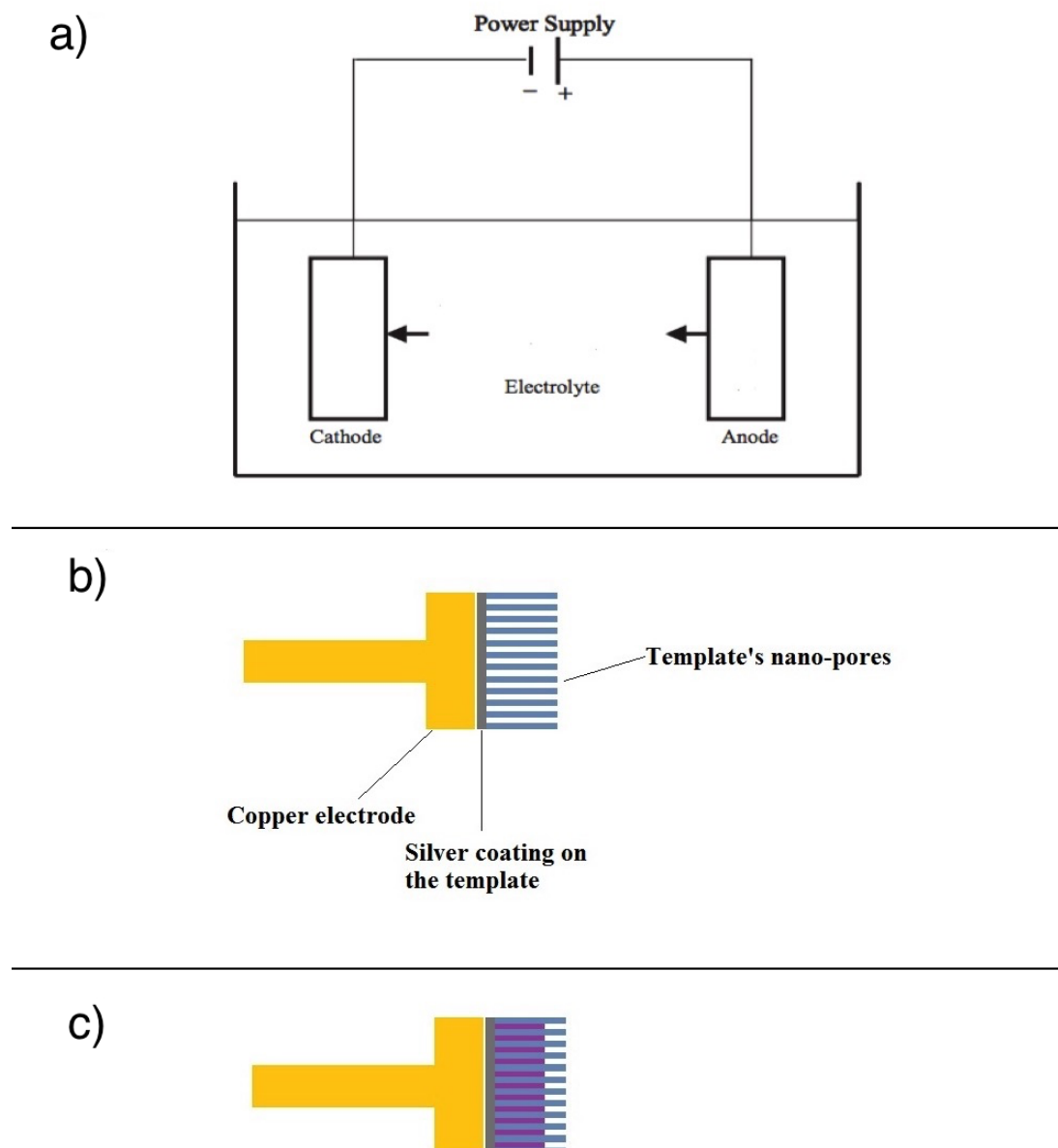


Figure 4.1: a) An illustration of the electrochemical deposition technique when b) a nanoporous template is placed at the cathode terminal, whereby c) metal ions from the electrolyte fill the pores.

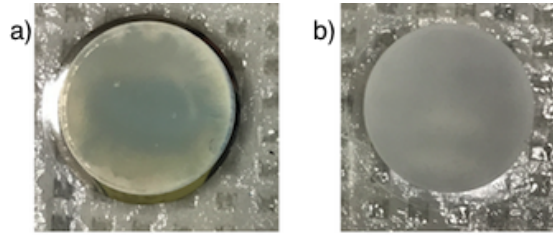


Figure 4.2: AAO membranes, a) coated with a 500 nm silver layer. b) AAO membrane without coating.

Since AAO membranes were made to serve as filters, shown in Figure 4.2 b, they must be coated with a conductive material for two reasons. The first reason is to make one face of the template conductive when placed at the cathode terminal to complete the electrical circuit. The second reason is to close off the membrane holes from one side to avoid solution leakage and deposition on the cathode metal surface instead of within the pores of the template. Therefore, a 500 nm layer of silver (Ag) was deposited to coat the membrane at one side, as seen in Figure 4.2 a.

A custom-made teflon cell is used for the electrodeposition process. Figure 4.3 shows the setup where the teflon cell contains the electrolyte, cathode, anode, and a reference electrode. A VersaSTAT 3 potentiostat-galvanostat from PAR was used to control the deposition process, as seen in Figure 4.3. In addition, VersaStudio software controls the VersaSTAT and tracks the amount of charge transferred. Further, it controls the applied over potential to excite the process. Typically, -400mV with respect to a reference electrode is applied through the anode, an optimal over potential value for rhodium (Rh) deposition determined by the experiments of Moghimian [57] for similar conditions.

4.1.1 Nanowires Used in This Work: Towards Transparent Electrodes

Rhodium NWs (RhNWs) have been produced using the electrodeposition technique for NW growth in AAO templates. 12.5mL of commercially available rhodium solution (Rh221D from Technic) diluted in 250 mL deionized (DI) water is used as an electrolyte. Based on a guiding plot for RhNW length provided by Moghimian [57], at least 120 Coulombs are needed to grow NW length in the range of 12-15 μm . Prior to rhodium deposition, silver was electrodeposited for 1 hour, to avoid material leakage and ensure that all pores in the AAO template are closed. In addition, silver

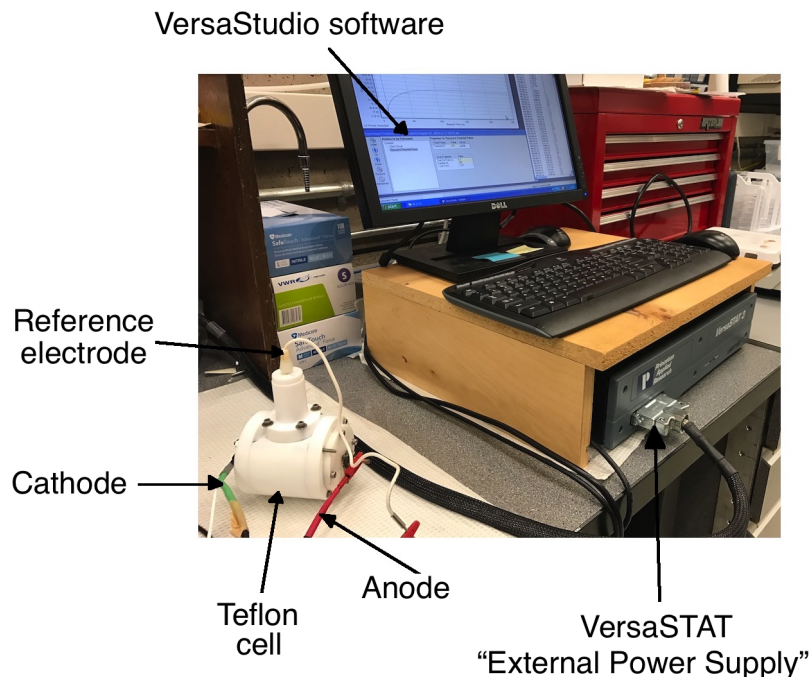


Figure 4.3: Electrochemical deposition setup used for synthesizing NWs.

deposition as an initial step was used to fill the branched region near one face of the AAO template. Following this, silver solution was replaced by the prepared rhodium solution. The deposition was run for 10 hours to pass at least 120 Coulombs.

After rinsing off the deposition solution, $5\mu\text{L}$ of nitric acid is dropped on the silver coated side of the template to dissolve both the silver coating and the short section of electrodeposited silver in the branched region of the nanopores. After that, the template is washed with DI water to remove impurities and dissolved silver. The process is repeated three times to ensure all silver content has been dissolved. Subsequently, the template is broken into three parts and each one is placed in a glass tube that contains a solution of 3MNaOH , to dissolve the AAO template. Glass tubes are sonicated for 15 minutes, then the solution is centrifuged to separate NWs from the solution. Finally, solution is replaced with DI water to wash the impurities (washing the NW patch with DI three times). NWs, freed from the template, were then suspended in ethanol, Figure 4.4.

The length and diameter of NWs has been measured using scanning electron microscope (SEM) images, as seen in Figure 4.5. The average length of NWs is close to $13\mu\text{m}$. This matches the guide plot provided by Moghimian [57]. Figure 4.5 shows SEM images of NWs used in this work. As seen in the figure, NWs have a

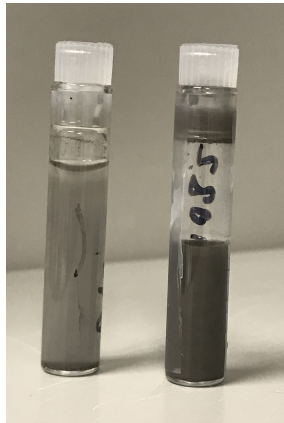


Figure 4.4: Diluted (left) and concentrated (right) RhNW suspensions.

good cylindrical uniformity; however, branching was observed for some NWs, which is mainly due to the AAO template. The branching does not affect the chaining process.

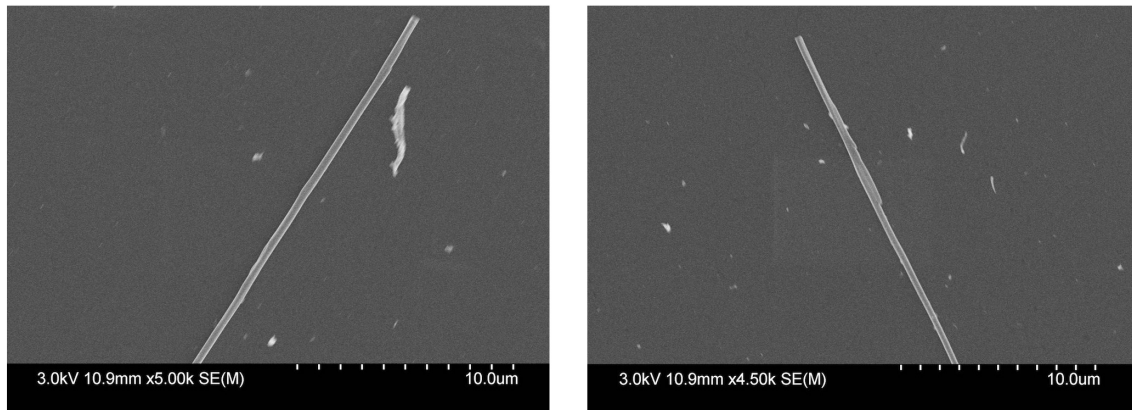


Figure 4.5: SEM images of NWs used in this work with an average length and diameter of 13 μm and 200nm, respectively. The SEM images show that the NWs have a good cylindrical uniformity.

4.1.2 Nanowire Concentration

Following the procedure of templates dissolution, we obtain a suspension of NWs that has an unknown NW concentration. How can we use this NW suspension to produce samples with desired NW concentration?

First of all, we would like to find the NW concentration of the original suspension. We diluted 100 μL from the original NW suspension with 1.5mL ethanol to produce a

diluted suspension. We produced such a diluted suspension to obtain accurate results of the counting process using ImageJ. Later, a 2 μL sample droplet from this diluted suspension was dropped on a microscope slide and allowed to dry. Several optical micrographs of the dried-out NWs were analyzed using ImageJ software. ImageJ is an open source software that is mainly used for color processing based on contrast and color threshold. The software features measurements of area, length and angles of a selection or of an entire image [58]. More importantly, it features particle counting, which was used to determine the number of NWs in an image. 80 images taken of the total area of NW suspension that dried out on a microscope slide were analyzed to count the total number of NWs available in the 2 μL droplet. Consequently, the concentration of the NW suspension was determined in the unit (NW/mL). This diluted suspension has a NW concentration of $7.1 \times 10^8 \text{ NW/mL}$. Using equation 4.1, we found that the original suspension has a NW concentration of $1.136 \times 10^{10} \text{ NW/mL}$.

We use equation 4.1 to produce NW suspensions with different concentrations as follows:

$$\nu_1.C_{NW1} = \nu_2.C_{NW2} \quad (4.1)$$

where ν_1 is the initial volume (100 μL) from original suspension, C_{NW1} is the NW concentration of the original suspension ($1.07 \times 10^{10} \text{ NW/mL}$), ν_2 is the volume of ethanol (1.5mL) that is always fixed, and C_{NW2} is the concentration of the desired NW suspension. Using equation 4.1, we can find the volume required from the original suspension (ν_1) to be diluted with 1.5 mL ethanol (ν_2) to produce the desired NW concentration (C_{NW2}). We produced seven NW concentrations using this equation, as listed in Table 4.1.

Table 4.1: Nanowire concentrations in a NW suspension used in this work

No.	Sample name	Concentration ($\times 10^8 \text{ NW/mL}$)
1	A	0.8
2	B	1.6
3	C	2.6
4	D	3.6
5	E	4.6
6	F	5.6
7	G	6.6

4.2 Micro-patterned Substrate Preparation

The main nanostructure driver, as discussed earlier in Chapter 3, is the micro-patterned substrate. The micro-patterned substrates were produced by photolithography, requiring a mask. The mask was designed by L-Edit software which provides tools for designing micro- and nanoscale structures. The design is then exported to a mask writer to produce the mask. The gold (Au) metal pattern was deposited on a glass substrate, with 2mm thickness, by photolithography, followed by a lift-off process. This yields a substrate with a 100nm thick Au pattern of interdigitated electrodes, as illustrated in Figure 4.6, with three assembly electrode gap sizes: $120\mu\text{m}$, $180\mu\text{m}$, and $240\mu\text{m}$ [45]. Further details on the process are available in Appendix A.

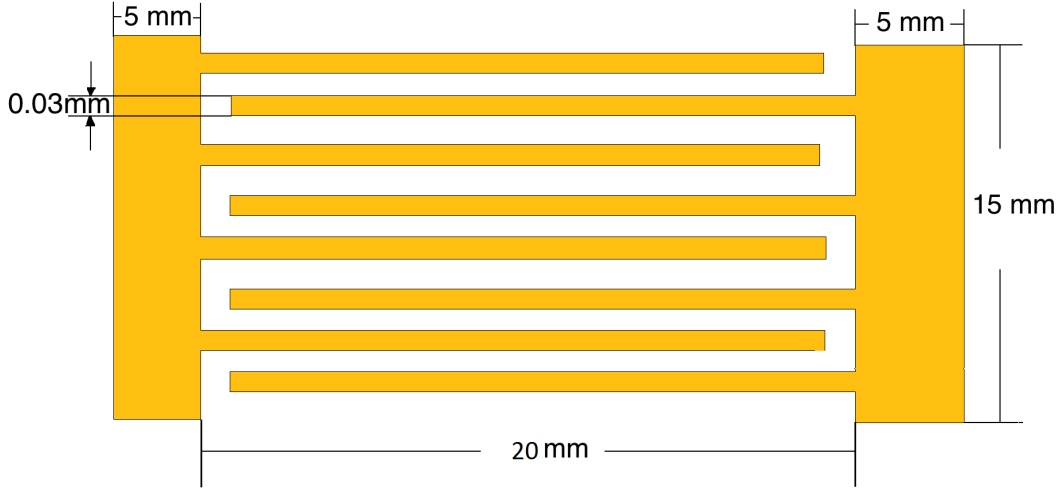


Figure 4.6: Schematic of interdigitated electrode substrate with a total width of 30 mm and height of 15 mm.

The effective area covered by the interdigitated electrodes, where the NWs are chained, has a fixed width of 20 mm but various lengths depending on assembly electrode gap size. Therefore, the number of assembly electrodes varies with different assembly electrode gap sizes. Table 4.2 lists the number of assembly electrodes in substrates with gap size of 120, 180, and $240\mu\text{m}$.

Table 4.2: Number of assembly electrodes in each substrate gap size

Gap size (μm)	Number of assembly electrodes
120	78
180	56
240	42

4.3 Measurements of Optical Transmittance

A Cary 50 UV-Vis spectrophotometer measures light transmittance using a dual light beam technique. The light beam passes through a splitter which splits the light into two beams. One beam goes directly to a silicon diode detector which measures the intensity (I_0) of the induced current by the light beam. The other light beam passes through the sample and then to another silicon diode detector. The current intensity (I) induced by the beam is measured after passing through the sample and the ratio between the two currents results in the transmittance value [59], which is expressed as:

$$T = \frac{I}{I_0} \quad (4.2)$$

The light beam at the focal length is of rectangular shape that is 0.71 mm wide and 1.13 mm high. Light transmission of the substrates with three different assembly electrode gap sizes (120, 180, and 240 μm) was measured. Substrates were mounted in the spectrophotometer such that assembly electrodes were in horizontal direction. Since the size of the light spot is much larger than the assembly electrode gap sizes, part of the light was absorbed and part of it scattered by several assembly electrodes. The number of electrodes that block the light could vary for different positions of the substrate. However, due to micron-size geometry, it is impossible to see how many of the assembly electrodes were blocking the light in each test. Therefore, several light transparency measurements were taken. The average of these measurements was considered to be the light transmission value of the substrate. There is a strong agreement with the calculated light transmission value, as shown in Table 4.3, with the measured value of plain substrates (no NW chains).

After NW-chain assembly using a dam, light transmission of the substrate was measured again. As before, substrates were mounted such that assembly electrodes were in a horizontal direction and NW chains were in a vertical direction. Using a

dam with wells of 1 mm width, it is possible that the light spot with 0.71 mm width either completely passes through NW chains or partially through the NW chains and the rest through the plane part of the substrate (the part between two adjacent wells). Therefore, to measure the light transmission of the substrate as accurately as possible, several readings from different part of the substrate were taken. The average of these numbers is reported as the light transparency. Substrate light transparency is the ratio of the open area to the total area. Therefore, light transmittance can be calculated as follows:

$$T = \frac{\text{Open area}}{\text{Total area}} \quad (4.3)$$

The width of a single assembly electrode (i.e., a gold bar) is 30 μm or 0.03mm. Within the image area the bar has an area of 0.0213 mm^2 (bar width 0.03mm $\times$ light beam width at focal point 0.71mm). Based on the pitch size, gap and an assembly electrode, the number of bars that are included in one measurement can be either at minimum or maximum. Several measurements taken with no NWs on substrate results in an average light transmission (T) value that strongly agrees with the calculated light transmission in Table 4.3. For gap sizes of 120 μm , 180 μm , and 240 μm , measured light transparency without NWs is 80%, 86%, and 89%, respectively.

Table 4.3: Calculated light transmission of the substrates

Substrate gap size (μm)	Pitch size (μm)	Minimum		Maximum		Average T (%)
		Number of bars	Calculated T (%)	Number of bars	Calculated T (%)	
120	150	7	81.4	8	78.8	80.1
180	210	5	85.37	6	84	85.37
240	270	4	90	5	86.75	88.37

The percentage of error in Cary 50 UV-Vis spectrophotometer is not reported in the specifications sheet [59]. Therefore, repeatability error was measured by taking several measurements at the same spot. A substrate without NW chains resulted in an estimate for maximum percentage error of $\pm 0.02\%$, whereas with NW chains the error is $\pm 1.5\%$ of transmission value. Higher light scattering by NWs is the main reason for a higher percentage of error with NWs on the substrate than without them.

4.4 Measurements of Electrical Resistance

The resistivity of a material (ρ) is a material property which illustrates the electrical resistivity of the material measured in ohm meter ($\Omega\cdot\text{m}$). The resistance (R) of material is reported as:

$$R = \frac{L\rho}{A} \quad (4.4)$$

where L is length and A is the cross sectional area of the material (width $\times$ thickness). However, to avoid material geometry calculation for reporting and comparing a resistance, the resistance at the surface of the conductive part (the sheet resistance) is reported instead. The sheet resistance is measured in Ω/square . It is reported for a dimensionless imaginary square on the surface to prevent involving three-dimensional geometry of the material. The sheet resistance (R_s) can be expressed as follows [60]:

$$R_s = \frac{\rho}{t} \quad (4.5)$$

where t is the material thickness. Since the cross sectional area is the product of thickness (t) and width (w), R_s can also be calculated by substituting equation 4.5 into equation 4.4 as follows [61]:

$$R_s = R \frac{w}{L} \quad (4.6)$$

The usual two point probe technique to measure the resistance of a material by multimeter may not be an accurate approach for measuring low resistances. When placing two probes on the surface of the substrate, they supply the current and measure the voltage drop at the same time. Due to probe contact with the substrate, a contact resistance is in series with the substrate resistance. As a result, higher resistance than the actual resistance of the substrate is reported [60]. The resistance caused by the leads is in series with the substrate resistance and contributes to the measured resistance. Therefore, a four-point probe measurement technique that eliminates these effects [60], is used to measure the electrical resistance accurately. The process involves two outer current probes and two inner voltage drop measurement probes, as illustrated in Figure 4.7.

There are different ways reported to measure the sheet resistance of a substrate, such as Van der Pauw method [62], Smits [63], and other techniques reported by Keywell 1960 [64]. Such techniques allow measuring the sheet resistance by directly placing the probes in a certain configuration. These techniques involve the shape and

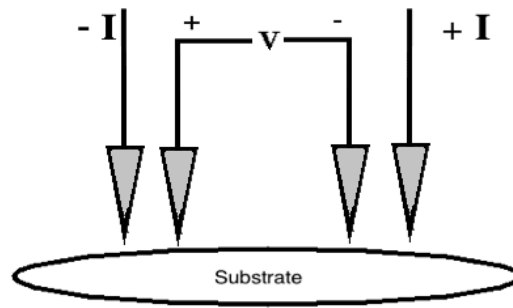


Figure 4.7: Illustration of four-point-probe. The distance between the current and voltage probes has to be minimized for accurate results.

geometry of the substrate and require various conditions. However, our substrates do not satisfy two of these conditions, which are:

- The substrate has insulated parts (not conductive); therefore, the surface is not singly connected.
- The substrates have a non-uniform conductive layer thickness since they are combining NW network and gold film, each of a different thickness.

As a result, none of the reported methods can be applied to our substrate since more than one of the conditions do not apply. Therefore, a different method is used to determine the sheet resistance of NW chain patch between a pair of assembly electrodes.

A Keithley 6340 source meter was connected to the four-point probe station. Figure 4.8 illustrates probe positioning for measuring (a) the resistance of each NW chain patch and (b) the resistance of the whole substrate. Probes with 15 to 25 μm tip diameter were placed on two assembly electrodes to measure the resistance of the patch of NW chains between them. Later, the resistance is substituted in equation 4.6 to find R_s of the NW chain patch. For each substrate, five to seven NW patches were sampled and their average resistance was taken to be the representative NW chain resistance for every patch on the substrate. Additionally, the total resistance of each substrate was measured to provide a general idea about the total resistance trend while varying NW concentration. The total resistance of each substrate was measured by placing a pair of current and voltage probes on the first large pad and another pair of probes on the second pad (Figure 4.8 (b)). Similarly, five measurements were taken from different positions along the pad to ensure accuracy. The sheet resistance measurement method has been used in accordance with the method of Kumar et al.

[61] for finding the sheet resistance of a NW network between two electrodes. This method was developed for evaluating conducting wire networks that is based on the geometry of the conductive part as in equation 4.6.

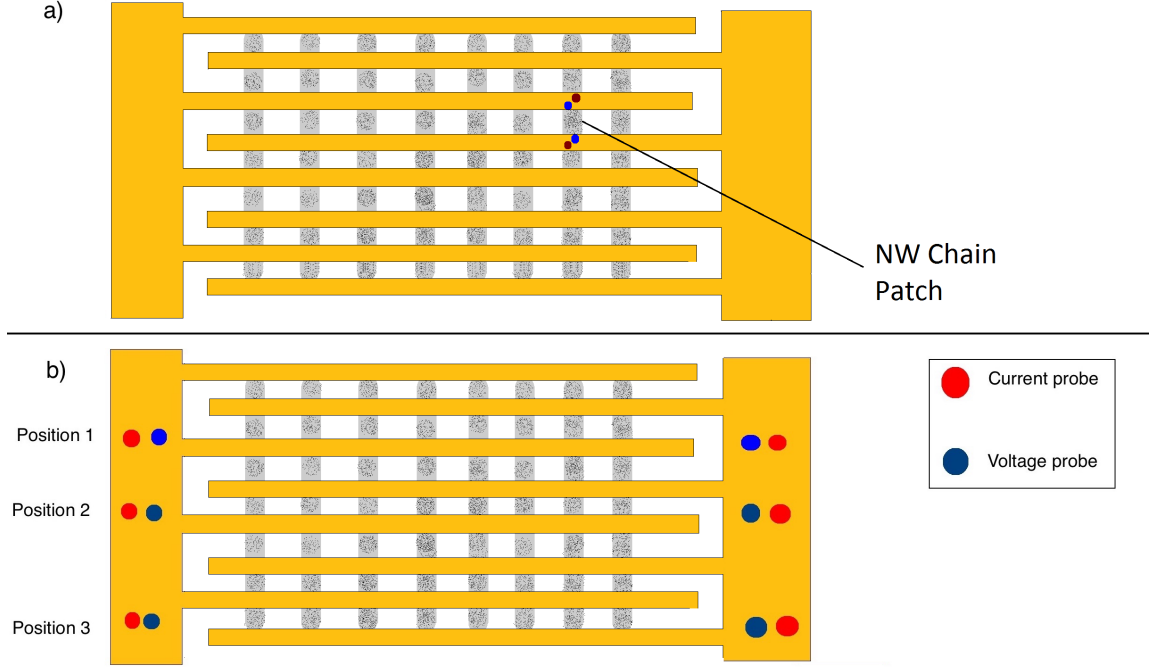


Figure 4.8: Illustration of probe positioning for measuring a) the resistance of NW chain patch, and b) the resistance of the whole substrate.

4.4.1 Correction Factor

While measuring the resistance of the NWs chain patch between two assembly electrodes (as illustrated in Figure 4.8 (a)), adjacent NW chain patches have an effect on the measurement since assembly electrodes connect them in parallel. The effect on the measured resistance has been investigated by measuring several NW chain patches within the substrate before and after isolation. The resistance of each NW chain patch was measured before isolation (R_1), then each patch was disconnected from adjacent NW patches by removing the connecting assembly electrode (i.e., the gold bar) by a scribe tool. Hence each patch of chained-NWs is isolated from the others. After that, the resistance of each patch was measured again after isolation (R_2). From the experimental results that was obtained by sacrificing a substrate, the change in resistance before and after isolation has been used as a correction factor

(R_2/R_1). We use the correction factor to avoid damaging other substrates in order to use them again.

We found that adjacent NW chain patches have a dramatic effect because of the parallel current paths. Adjacent NW chains decrease the measured resistance by $\approx 50\%$ of the actual resistance of the NW-chains patch. Hence, once the NW chain patch is measured (as in Figure 4.8 (a)), it must be multiplied by a correction factor of 2 to get the correct value of the resistance. Thus, correction factor eliminates the effect of adjacent NW chain patches and helps in preserving the substrate for further use without getting it damaged. Further information on verification of correction factor number is available in Appendix A.8.

4.5 Nanowire Chaining Process

As previously discussed in Chapter 3, a non-uniform electric field is required to use DEP force. To create NW chains, we use an AC function generator which is connected to the patterned substrate. An AC electric field is required to keep a strong-dipole NW to create NW chains. The ions and the polar molecules in the NW suspension medium may screen the NWs causing them to depolarize if the frequency of the AC field lower the relaxation frequency of ions and polar molecules.

In the following subsections, the experimental setup is discussed, and the applied parameters are reported.

4.5.1 Experimental Setup for NW-Chaining

In this work, probes in the probe station were connected to Tektronix CFG253 function generator. In order to control the applied frequency and voltage, Tektronix DMM4050 multimeter was connected to the function generator. As shown in Figure 4.9, probes were placed on large pads while the chaining dam is placed on the interdigitated electrode area.

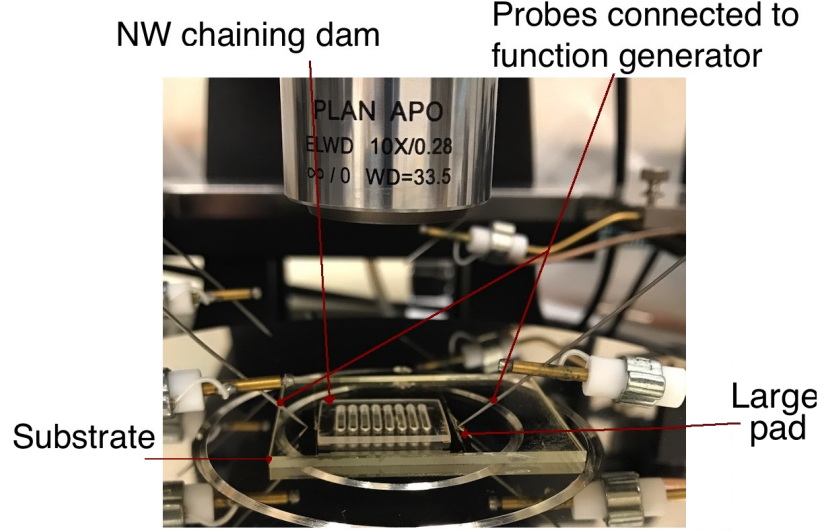


Figure 4.9: NW chaining setup. The NW chaining dam is placed on the interdigitated electrode area in the substrate, while the probes, that are connected to the function generator, are placed on the large pads on the substrate.

4.5.2 Experimental Process and Applied Parameters

For each gap size, seven substrates have been used to chain NWs from seven NW suspensions of different concentrations, listed in Table 4.1. From each NW suspension, a volume of $80 \mu\text{L}$ was introduced to each substrate with a gap size of 120, 180, and $240 \mu\text{m}$.

To investigate the effects of NW concentration and the electric field on NW chaining, two sets of experiments were performed. First, fixed voltage (5 V) was applied for all substrate gap sizes, which results in different electric field strengths between assembly electrodes for different substrates, as listed in Table 4.4. A measure of the electric field strength is defined as follows:

$$E = \frac{V}{d} \quad (4.7)$$

where V is the applied voltage, and d is the distance between assembly electrodes in meters. The electric field strength is measured in (V/m) . In a second set of experiments, the electric field strength was fixed among all gap size substrates by adjusting the applied voltage. Maximum V_{rms} available to us is 7 volts. Therefore, based on the maximum voltage applied on the largest gap size substrate in this work, electric field strength was fixed at $29.2 \text{ kV}/\text{m}$.

Table 4.4: Applied voltages and their corresponding electric field

Substrate gap size (μm)	Fixed applied voltage (V)		Fixed electric field (E)	
	(V)	E (kV/m)	(V)	E (kV/m)
120	5	41.7	3.5	29.2
180	5	27.8	5.25	29.2
240	5	20.8	7	29.2

4.6 Concluding Remarks

In this chapter, we discussed the experimental set-up for NW synthesis, micropatterned substrates, and the NW chaining setup. In addition, we discussed the tools used for the measurements of optical and electrical properties. As discussed, the process involves cost-effective approaches as well as simple tools. NWs with an average length of $13\ \mu\text{m}$ and diameter $\approx 200\ \text{nm}$, were synthesized by the electrodeposition technique. From the main NW suspension, seven different NW concentrations were produced ranging from 0.8 to $6.6 \times 10^8\ \text{NW/mL}$, listed in Table 4.1. In addition, three types of micron-patterned substrates were used in this work. Each substrate has a unique gap size of 120 , 180 or $240\ \mu\text{m}$, fabricated by the photolithography technique followed by lift-off process. Moreover, optical properties of the substrates were measured using Cary-50 UV-Vis spectrophotometer which has a repeatability error of $1.5\ \%$ of the light transmission value. Further, electrical properties of substrates were measured using the four-point probe technique to eliminate probe contact resistance. We also illustrated the position of current and voltage probes for such measurements. A correction factor was found to be 2 and is necessary to be multiply the measured resistance values of NW chain patch. The correction factor is important since it eliminates the effect of adjacent NW chains patches that are connected in parallel.

Chapter 5

Measured Electrical and Optical Performance of NW-Chained Transparent Electrodes

The performance of TEs is evaluated by a Figure of Merit (FoM) based on the measured optical transmittance and electrical resistance. The FoM is used to compare the performance of transparent electrodes. This chapter presents the results of measurements of electrical and optical properties, using the methods outlined in Chapter 4. In addition, we use the measurements to discuss the effects of NW assembly parameters on optical and electrical properties.

5.1 Optical and Electrical Performance

Light transparency and electrical sheet resistance of substrates with different gap sizes of 120, 180, and 240 μm , that have NW chains from various NW suspension concentrations listed in Table 5.1, have been measured and are discussed in the following sections.

Table 5.1: Nanowire concentrations in a NW suspension used in this work

No.	Sample name	Concentration ($\times 10^8$ NW/mL)
1	A	0.8
2	B	1.6
3	C	2.6
4	D	3.6
5	E	4.6
6	F	5.6
7	G	6.6

5.1.1 Device Transparency

Light transmission depends on the open area, which is the area of the substrate not covered by the interdigitated electrodes and NW chains. If the spaces between NWs in the chained areas pass no light, the transparency of TEs should be expected to increase linearly with increasing percentage of the open area. The photolithographically patterned thin film electrodes required for NW chaining impose a blockage that is fixed after the choice of electrode width and gap size, as was presented in Table 4.3. Before NW chaining, light transmission of the substrates with three different assembly electrode gap sizes of 120, 180, and 240 μm was measured as 80, 86, and 89% respectively, shown in Figure 5.1. We used different concentrations of NWs for NW chaining and expected a monotonical decrease in light transmission by increasing the concentration of NWs. Figure 5.1 shows that a decrease is observed while increasing the concentration from 0.8 to $2.6 \times 10^8 \text{ NW/mL}$ and from 4.6 to $6.6 \times 10^8 \text{ NW/mL}$, but transmission is almost constant or shows a slight increase at concentrations in between these ranges.

However, we find that the fraction of the starting open area covered by NW chains does not change linearly with NW concentration. In fact, light transmission increases from NW concentration 3.6 to $4.6 \times 10^8 \text{ NW/mL}$, due to gaps appearing between NW chains, as seen in Figure 5.2. A plausible reason suggested by Figure 5.2 could be dipole-dipole interaction between NWs of neighboring chains, if the separation distance between the chains becomes small. We will name this neighbor-interaction.

The light transmission variation with concentration can be reasonably fitted by a cubic polynomial curve, as shown in Figure 5.1. As clearly seen in Equations 5.1 and 5.2 below, the equations for the best fit curves for substrates with 120 and 180 μm gap size are seen to have the same shape and differ by a constant value 6.3, independent

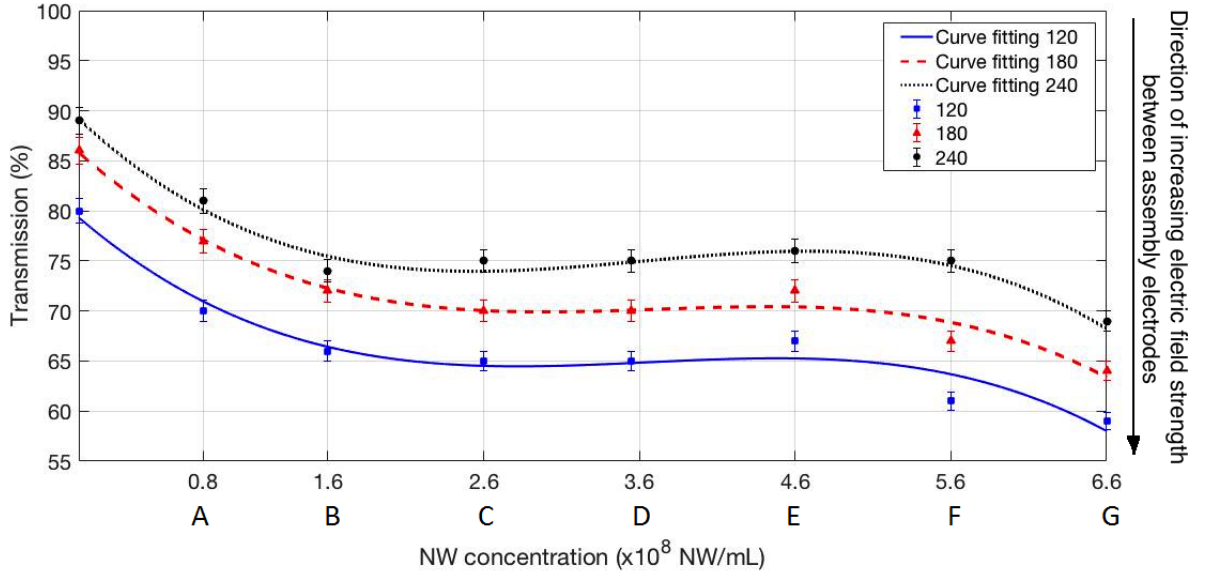


Figure 5.1: Light transmission experimental results and best fitting curve for each substrate plotted against NW concentration, including error margin of each point, that is 1.5% of T value. NWs were chained with the applied voltage (5 V) fixed for all gap sizes.

of concentration x :

$$T_{120} = 79.3 - (13.33x) + (3.85x^2) - (0.35x^3) \quad (5.1)$$

and

$$T_{180} = 85.8 - (13.33x) + (3.85x^2) - (0.35x^3) \quad (5.2)$$

Here, T_{120} and T_{180} are the transmission for two gap sizes 120, and 180 μm , respectively, and x is the NW concentration.

On the other hand, the light transmission for the substrate with 240 μm gap size, though also well fit by a cubic polynomial, has different coefficients given by:

$$T_{240} = 89 - (14.61x) + (4.44x^2) - (0.41x^3) \quad (5.3)$$

Interpreting Figure 5.1, at low NW concentrations there is an insufficient number of NWs resulting in few chains being formed. Thus, less area is covered with NWs resulting in high light transmission. However, at concentration E, higher transmission is observed than at concentrations B to D, which is a result of the large gap between chains. Device light transmission from NW concentration E to G decreases with NW

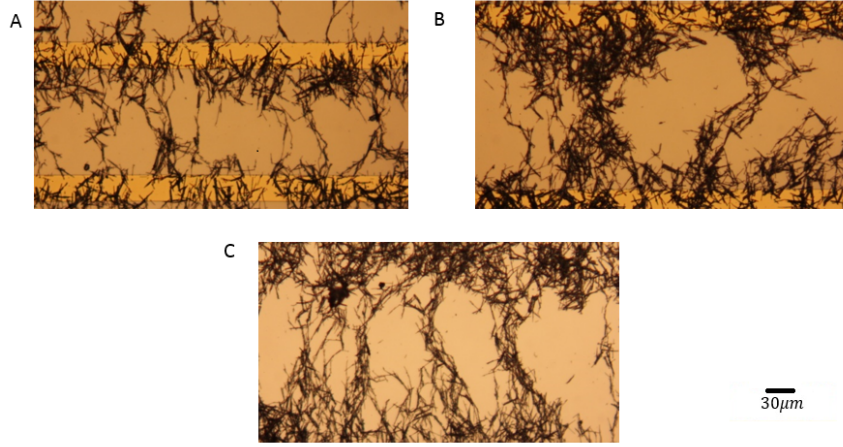


Figure 5.2: Optical microscope images of substrates a)120 μm , b)180 μm and c)240 μm , with NW chains from suspension E, $4.6 \times 10^8 \text{ NW/mL}$, that clearly show the appearing gap between NW chains that affects the light transmission.

concentration increase, as maybe expected, due to coverage of the open area.

Figure 5.1 has been replotted and divided into four regions, 1, 2, 3, and 4 based on their light transmission behaviors that was observed while varying NW concentrations. Yellow shaded areas, 1 and 4, in Figure 5.3 have approximately the same curve trend. Light transmission in the white area, number 2, remains constant between the two concentrations C and D, although NW density increased. From the series of microscope optical images for each of the concentrations A through G in Table 5.1 seen in Figure 5.4, the chaining behavior changes with increasing NW concentration. NWs accumulate adjacent to the assembly electrodes and less NWs accumulate in the middle of the gap of the assembly electrodes creating a double triangle structure. Due to this behavior, the total open area remains the same although NW concentration increased from C to D. This behavior explains the constant light transmission in this region. However, in the green area, number 3, starting at NW concentration E, the light transmission is slightly higher than concentration D (i.e., $4.6 \times 10^8 \text{ NW/mL}$) in all substrates. The ratio of open area increases, as seen in Figure 5.4 D and E whereby the NWs are clumping together in this concentration range, which results in increase in light transmission from concentration D to E. This clumping maybe due to neighbor-interaction and the capillary force of the drying front. Change in light transmission in this region must be accounted for, since the change is higher than error margins in previous concentrations. Beyond this, in region 4 in Figure 5.3, maybe explained by NW filling in the gaps seen in the micrograph for concentration

E, Figure 5.4 E and F. This results in a decline in light transmission.

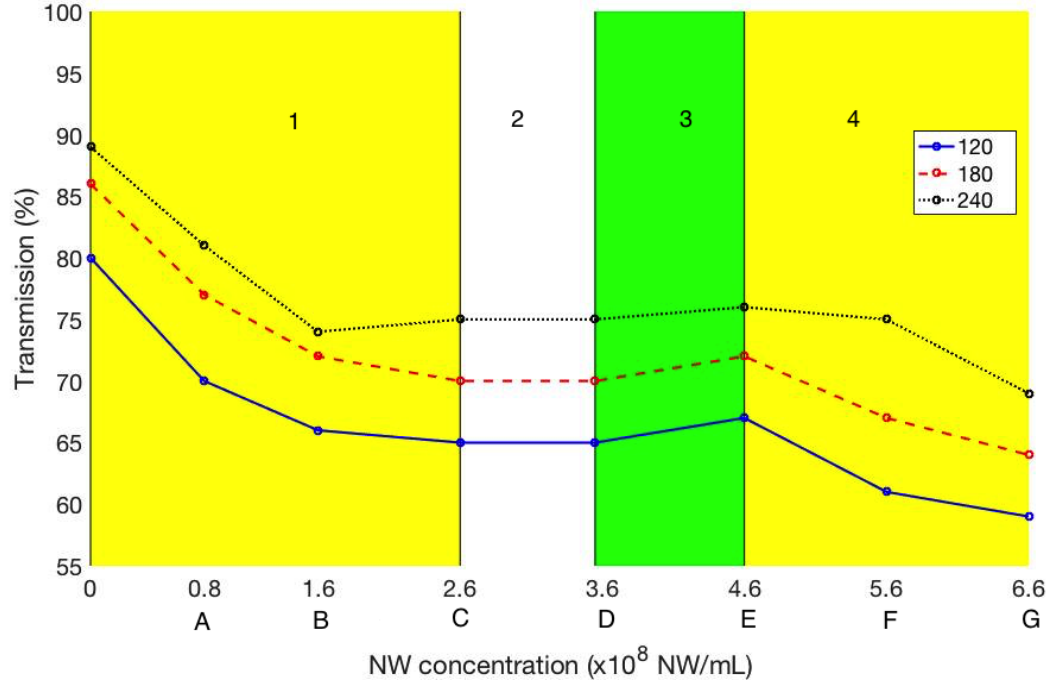


Figure 5.3: Light transmission versus NW concentration. Region 1 covers NW concentration from 0 to 2.6×10^8 NW/mL and region 4 covers NW concentration from 4.6 to 6.6×10^8 NW/mL have similar curve trend, whereas region 2 light transmission is constant between concentrations 2.6 and 3.6×10^8 NW/mL, and region 3 light transmission increases by approximately 2 %.

With the choice of well-width and pitch for the process dam wells, discussed earlier in chapter 4, the areas covered with NWs are still only a fraction (in our case 50%) of the total area in which chains could have been formed. For the three gap sizes 120, 180, and 240 μm the minimum open areas are 40, 43, and 45 %, respectively.

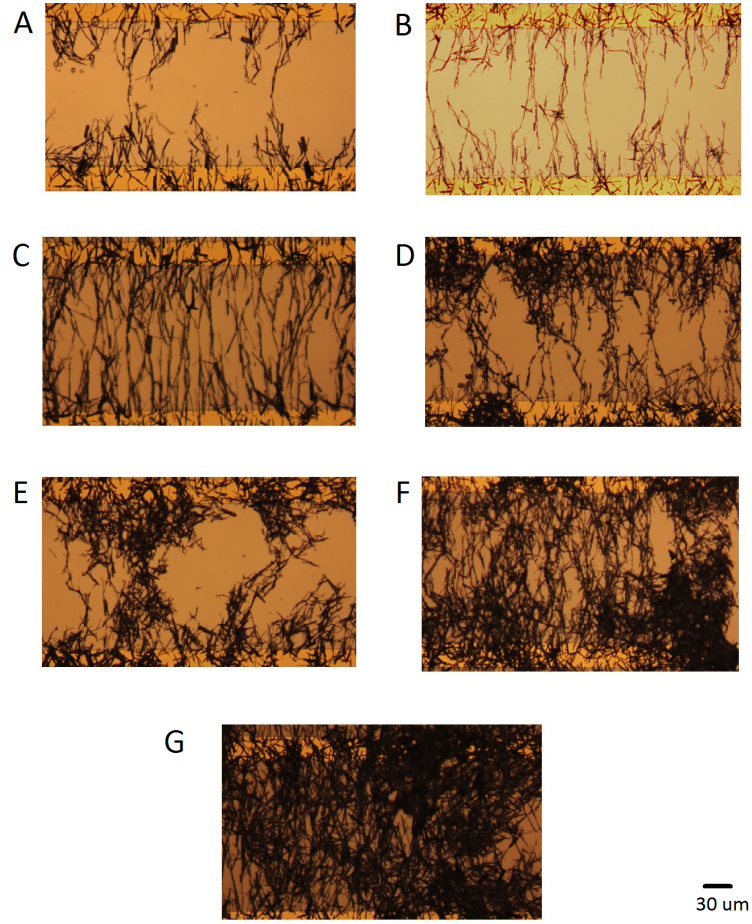


Figure 5.4: Optical micrographs of 180 μm gap size substrate chained with concentrations A, B, C, D, E, F, and G, chained with fixed applied voltage, 5 V, that shows the effect of increasing NW concentration.

5.1.2 Device Electrical Properties

In this section, we present and discuss results related to the low sheet resistance achieved by our use of chained-NW TEs. Using a constant voltage would produce different nominal electric field strengths ($=\text{voltage}/\text{gap size}$) for substrates with different gap sizes. Would this affect the total resistance due to the nature of chaining?

To understand this, we measured the total resistance (R) of each substrate by the four-point probe technique, as shown in Figure 4.8 b. The total resistance is plotted against the corresponding nanowire concentration in Figure 5.5. As presented, we see that samples with the lowest resistance are expected to be those of the smallest gap size chained using the highest NW concentration. In addition, as seen in Figure 5.5, the substrate with the largest gap (240 μm) chained with NW concentration B has

a total resistance of $11\ \Omega$, whereas the substrate with the smallest gap size, $120\mu\text{m}$, chained using the highest NW concentration, G, shows the least resistance among samples as may be expected, reaching about $3.5\ \Omega$.

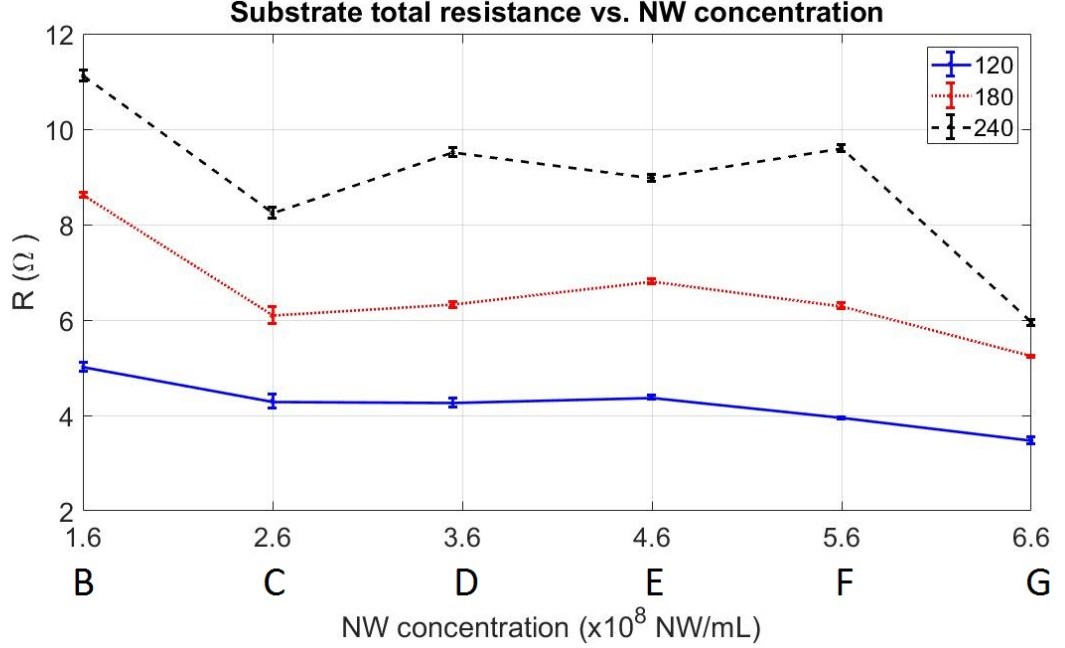


Figure 5.5: Substrate total resistance versus NW concentration. Overall decrease in total resistance when increasing NW density, while the electric field is varying between assembly electrode (i.e., fixed applied voltage 5V across gap sizes of 120, 180, and $240\ \mu\text{m}$).

From Figure 5.5, the increase of total resistance between concentrations D and E, corresponds to fewer chains with larger spacing as observed from the micrograph in Figure 5.4 D and E. The gap results in lower density of chains connected in parallel; hence, higher total resistance as shown in the schematic in Figure 5.6 a and b. Assuming that each chain resistance is R , then the total resistance in schematic (a) in Figure 5.6 is less than the total resistance in schematic (b).

With a larger gap size of $240\mu\text{m}$, we have less control of NW chains due to the low nominal electric field strength. Hence, randomness of NW chains occurs. As a result, resistance curve behavior varies with NW concentration in the interval $x=[2.6, 5.6] \times 10^8 \text{NW/mL}$. Owing to the large gap size, each NW chain patch starts out being thick from the assembly electrode, where F_{DEP} is dominant, and thins out towards the middle of the gap, as seen in Figure 5.6.

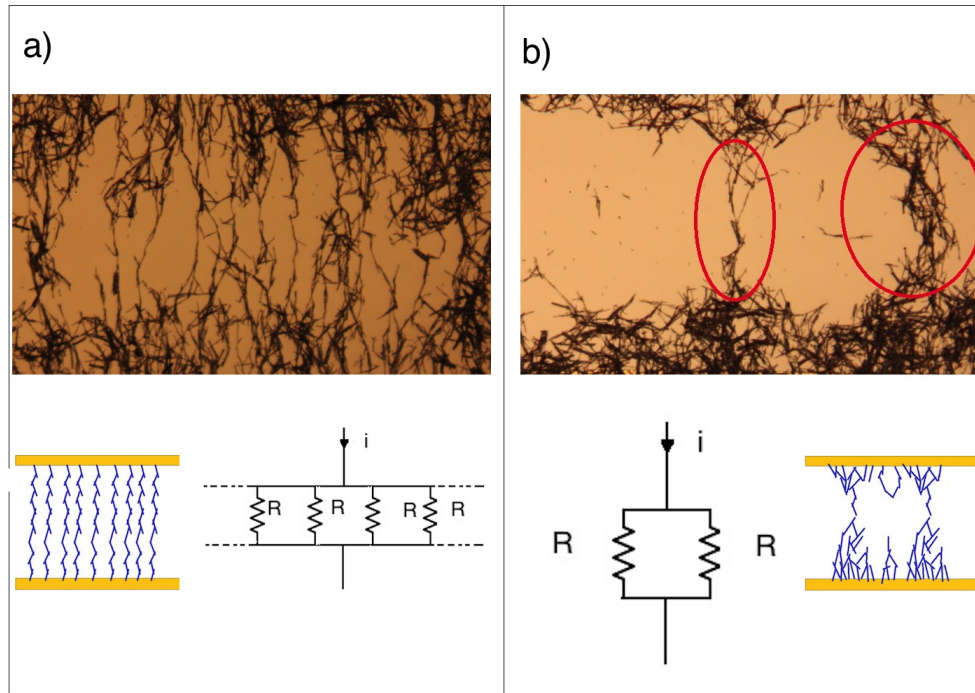


Figure 5.6: a) Several parallel NW chains in $240\ \mu\text{m}$ gap size substrate, chained from NW concentration C, $2.6 \times 10^8\ \text{NW/mL}$, and b) two NW chains between two assembly electrode using NW concentration D, $3.6 \times 10^8\ \text{NW/mL}$, dramatically affect the resistance. Below each, a schematic of the chains as resistors connected in parallel and their equivalent are represented by an electrical circuit.

The resistance of a patch of nanowire chains between a pair of assembly electrodes (R_{patch}) has been measured, as previously illustrated in Figure 4.8 (a), and plotted versus the corresponding NW concentration in Figure A.1. The main motivation for such measurements is to calculate the sheet resistance (R_s), the most commonly used parameter for comparison in the literature. We use equation 4.6, with $w=1\text{mm}$ as the chaining dam-width, and L the electrode gap size. R_{patch} has been multiplied by the correction factor (2), as discussed earlier in Section 4.4.1, then substituted in R in equation 4.6. The calculated sheet resistance is plotted versus the corresponding concentration in Figure 5.7.

The overall trend shows sheet resistance decreases with increasing NW concentration due to conductivity enhancement in the patch, as a result of extra NWs added. However, sheet resistance varies for the case of NW concentrations B and C, due to variation of inter-chain gap size. The highest R_s among substrates is $880\ \Omega/\text{sq}$ for very sparse chains (Figure 5.4b). Interestingly, all substrates at maximum concen-

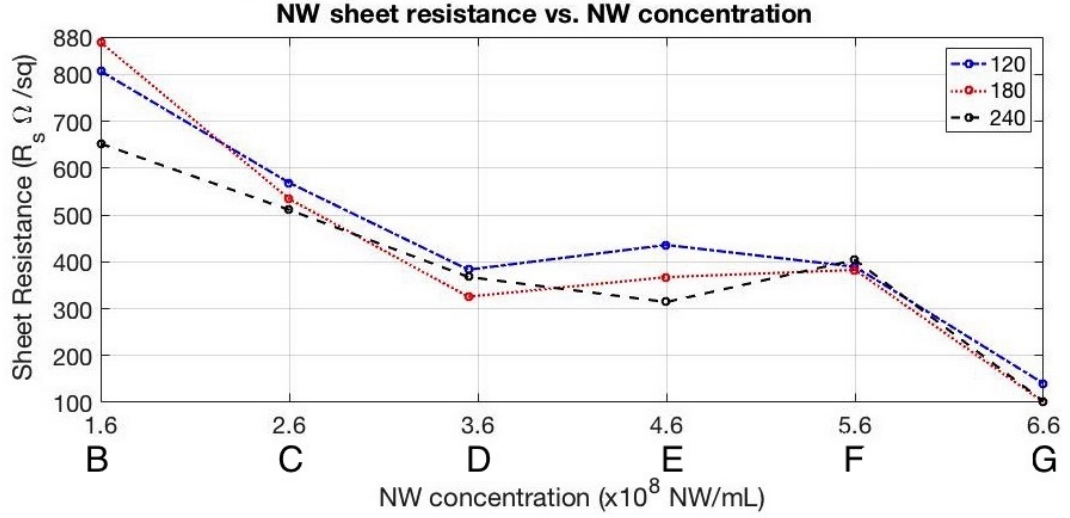


Figure 5.7: Sheet resistance of the chained-NW patch measured at various NW concentrations and three electrode gap sizes. Overall the plot shows a decrease in sheet resistance with increasing NW concentration. Larger variation in sheet resistance between the three substrates at concentration 4.6×10^8 NW/mL is correlated to variation in inter-chain spacing.

tration (G) have R_s as low as $100 \Omega/\text{sq}$, which is within the range seen for ITO, the best available material.

We may ask, why R_s is different in the concentration range D to E in Figure 5.7. This may be understood by looking at the micrograph Figure 5.4 D and E. The clumping becomes more pronounced from D to E, showing that NWs gather into structures where they are not useful in reducing the resistance. The narrow neck in the double triangle structure in E dominates the resistance, and the larger number of NW used up in making the triangle bases do not significantly reduce the resistance. This process continues from concentration E to F. From F to G, NWs begin to fill in the smaller gaps and become effective in decreasing the resistance through a new mode.

Further improvement over our sheet resistance value $100 \Omega/\text{sq}$ certainly seems possible by efforts to reduce NW-NW contact resistance (R_c). Song et al. [65] have demonstrated the significance of such resistance and concluded that R_c is much greater than NW resistance (R_{NW})[65].

It is worth noting that substrates with NW chains from very low concentration A ($0.8 \times 10^8 \text{ NW/mL}$) have infrequent chaining, resulting in low and variable electrical conductance. Therefore, such concentrations have been determined to be unsuitable for TE application.

5.2 Measurements of Nanowire Chain Quality

Within the NW chaining area, there are NW chains that are functional and connect the two assembly electrodes. On the other hand, nonfunctional NW chains that form part of a bridge between electrodes are present as well. They block the light without being beneficial to enhance electrical conductance, as seen in Figure A.2. Therefore, further analysis was carried out to investigate the fraction of functional NW chains. The measurement was performed by using ImageJ software, which involves measuring the areas covered by the nonfunctional and functional NW chains. The fraction of functional NW chains based on the area they cover is plotted versus NW concentration, as seen in Figure 5.8.

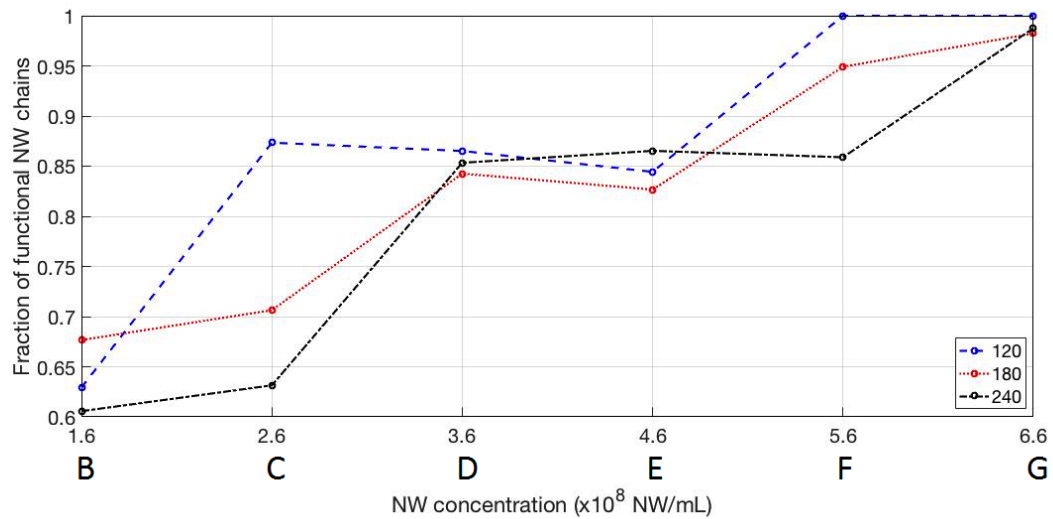


Figure 5.8: Fraction of functional NW chains increases when increasing NW concentration. NWs are chained using constant applied voltage (5 V) on all gap sizes.

From Figure 5.8, it can be concluded that high NW concentration increases the fraction significantly. Additionally, chaining NWs at small gap size, $120\mu\text{m}$, results in maximum fraction of functional NW chains among all substrates in all NW concentrations. In fact, the fraction is as high as 1 at high NW concentrations, F and G. Overall, the average fraction of functional NW chains in all substrates is 0.83. Increasing the fraction would enhance the performance of the device. Admittedly, increasing NW concentration plays an important role in increasing the fraction of functional NW chains, yet, it leads to light transmission reduction as well.

The two main parameters that determine the efficiency of substrates are transparency and sheet resistance. We define the transparency parameter as:

$$T = 1 - \frac{(A_{\text{assembly elec.}} + A_{FNW} + A_{NFNW})}{A_{\text{total}}} \quad (5.4)$$

where A_{total} is the total area of substrate, $A_{\text{Assembly elec.}}$ the area covered by the assembly electrode, and A_{FNW} and A_{NFNW} are the areas covered by functional and non-functional NW chains, respectively. However, there are two approaches to increase light transmission while maintaining electrical properties, or even enhance them, by:

- Reducing already-opaque assembly electrode width while increasing its thickness, to reduce the light-blockage area while increasing its electrical conductance;
- Increasing the fraction of functional NW chains.

The first requires redesigning the pattern of substrate (another design is discussed later in section 6.2). However, the second can be achieved by two options. First, NW concentration can be increased; however, this option decreases light transmission. Second, the electric field strength can be manipulated. The effects of the electric field strength, discussed in the section 5.3 below, contribute to the quality of NW chains.

5.3 The Effects of Electric Field

NW concentrations C and E, 2.6 and $4.6 \times 10^8 \text{NW/mL}$, have been used to create chains for all three gap sizes. However, when the voltage was adjusted to fix the nominal electric field strength at 29.2 kV/m for all gap sizes on substrates, as presented in Table 4.4, it was found that this high electric field strength increases the

fraction of functional NW chains as listed in Table 5.2, when compared with data in Figure 5.8. Hence, better NW chaining control is obtained at high electric field strength, as seen in the optical micrographs provided in Appendix A.3.

Table 5.2: Fraction of functional NW chains for all three gap sizes, with chains made from NW concentration C and E, while electric field is fixed at 29.2 kV/m

Substrate gap size μm	NW suspension concentration ($\times 10^8 \text{NW/mL}$)	NW suspension label	Fraction of functional NW chains
120	2.6	C	0.80
	4.6	E	0.66
180	2.6	C	0.85
	4.6	E	0.84
240	2.6	C	0.84
	4.6	E	0.89

Electrical and optical properties of substrates with NWs chained using a fixed electric field strength have been measured as well. The results agree with the statement that better NW chain control is obtained at higher electric field strength. In addition, results show an increase in optical transparency when higher electric field is present, in comparison to data in Figure 5.1. At higher electric field strength, T increased by 3 % for substrate gap sizes 180 and 240 μm . Although the transparency for the substrate gap size 120 μm increased as well, this increase is small and within the error associated with the measurements, that is 1.5% of transmission value.

Table 5.3: Sheet resistance R_s of substrates 120, 180, and 240 μm with NW chains from concentrations C and E using fixed electric field, 29.2 kV/m

Substrate gap size μm	NW suspension concentration ($\times 10^8 \text{NW/mL}$)	NW suspension label	R_s (Ω/sq)
120	2.6	C	830.12
	4.6	E	710.79
180	2.6	C	518.09
	4.6	E	394.49
240	2.6	C	483.67
	4.6	E	314.94

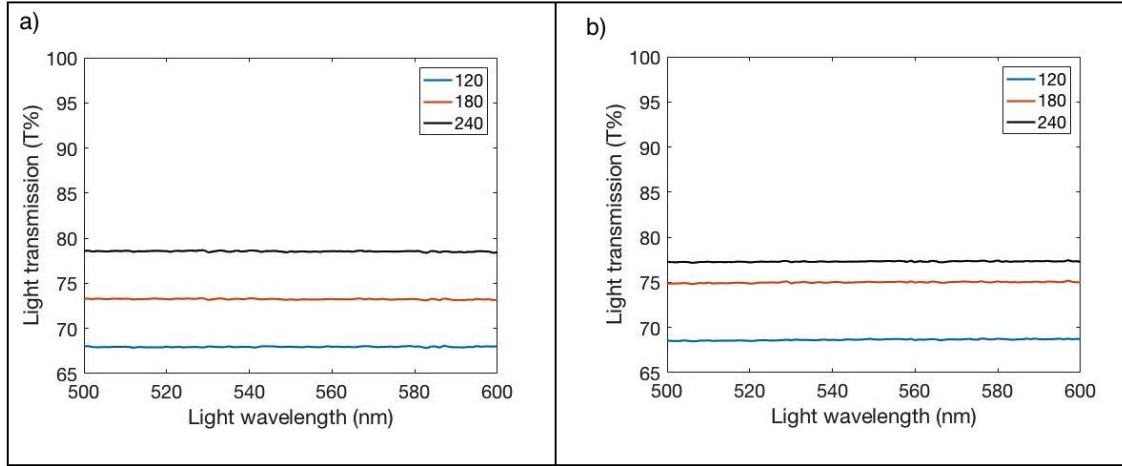


Figure 5.9: Optical transparency of substrates 120, 180 and 240 μm gap size, while chaining NWs from concentration a) $2.6 \times 10^8 \text{ NW/mL}$ and b) $4.6 \times 10^8 \text{ NW/mL}$, using fixed electric field (29.2 kV/m).

In addition, sheet resistance of NW chains decreases at higher nominal electric field strength. The sheet resistance of NW chains, as presented in Table 5.3, are lower than in case of using low electric field strength, as seen in Figure 5.7.

5.4 EDL Presence

The electrical double layer (EDL) has a significant effect on the NW chaining process, as discussed earlier in Chapter 3. One possible advantage of the EDL being present around the NW during the assembly process is that it may explain why NWs hover above the electrode. Hovering allows the assembly of multiple chains, without the first chain shorting out the electrodes. The repulsive force caused by the EDLs around the NWs and the assembly electrode could explain why they hover above the assembly electrode.

Freer et al.[66] and Sam et al. [45] have used dielectrophoretic force (F_{DEP}) for single NW assembly. Both report that repulsion between NW and substrate surface does occur. Otherwise, the NW will adhere to the substrate surface or to the assembly electrode due to van der Waals attraction [66]. However, total forces illustrated in Figure 5.10 (EDL repulsive force, gravitational force and DEP force) could sum to near-zero, which may explain why the NWs hover above the substrate. Once the alcohol evaporates, EDL starts to decrease, allowing all NWs to sit at once on the entire substrate, including the assembly electrodes.

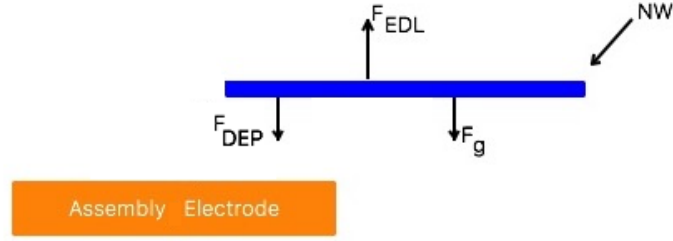


Figure 5.10: Forces acting on nanowire.

5.5 Comparison and Evaluation

In order to evaluate and make a comparison between the available TEs, a Figure of Merit (FoM) is used to represent their performance. A higher number for FoM represents a better performing TE. FoM is a ratio of transparency to sheet resistance. There are two FoM equations that relate optical transmittance and sheet resistance. The first equation is the ratio of DC conductivity to optical conductivity as follows [35].

$$\frac{\sigma_{D.C.}}{\sigma_{Optical}} = \frac{188.5}{R_s(T^{-\frac{1}{2}} - 1)} \quad (5.5)$$

where 188.5 is half the value of the impedance of free space, $Z_0 = 377\Omega$. FoM defined by using equation 5.5 is used for thin and uniform conductive layers [67]. In addition, $\sigma_{D.C.}/\sigma_{Optical}$ is highly dependent on the conductive layer thickness as well as the material's DC conductivity, which decreases when thickness decreases below a threshold [68].

In this work, neither the NW network thickness nor the substrate are uniform, due to the presence of NW-free areas caused by the dam. The alternative equation 5.6 below, is preferred for calculation of FoM. FoM in equation 5.6 is reported by Haacke [3] who related substrate light transmission to its sheet resistance (Ω^{-1}). Haacke's FoM is calculated as follows:

$$\phi_H = \frac{T^{10}}{R_s} \quad (5.6)$$

T raised to the power of 10 has been selected to correct the transparency value at minimum conductive layer thickness, as discussed in Appendix A.5. The results have been tabled in the Table A.1 located in Appendix A.4. FoM calculated based on equation 5.6 shows that the substrate with largest gap size $240\mu\text{m}$ and chained

with NW concentration G, i.e., the highest NW concentration, has the highest FoM, $2.39 \times 10^{-4} \Omega^{-1}$. Among all substrates, this substrate has a relatively high light transmission of 69%, and low R_s of $102.5 \Omega/\text{sq}$. Although $240\mu\text{m}$ with concentration E results in better light transmission, up to 76 %, sheet resistance is much higher for concentration G. Similarly, when chaining while applying high voltage, 7 volts, light transmission reached 78%. On the other hand, the lowest FoM among all samples was found to be for the smallest gap size substrate chained with relatively high NW concentration, i.e., $120\mu\text{m}$ chained with concentration F, has FoM of $1.83 \times 10^{-5} \Omega^{-1}$.

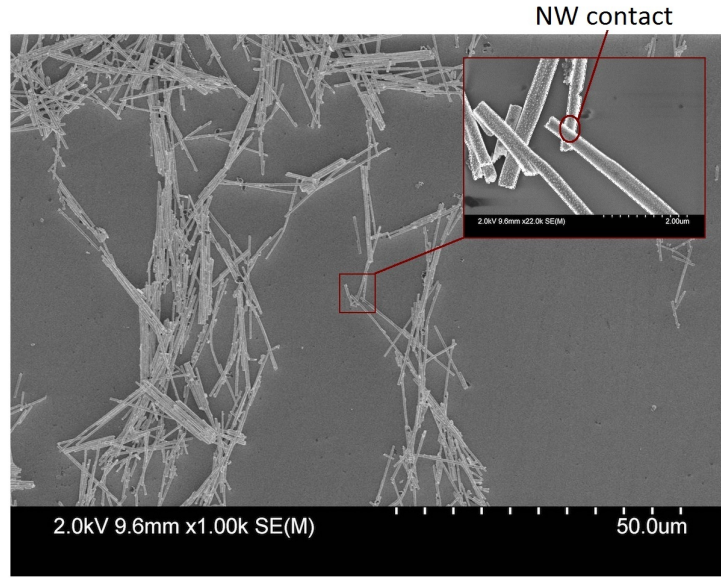


Figure 5.11: SEM image of NW-NW contact.

Maximum FoM in this work has exceeded the FoM of another approach that uses multilayer films [69]. The approach still uses ITO. However, in order to reduce ITO consumption and increase the transparent electrode conductivity a thin metal layer is sandwiched between the ITO layers, ITO/metal/ITO. Copper, with a thickness of $\approx 16\text{nm}$, has been used as a sandwiched metal layer and it has been reported that it has a maximum FoM of $5.2 \times 10^{-5} \Omega^{-1}$ [70]. Moreover, the highest FoM in this work is comparable to another alternative such single layer of graphene, listed in Table 5.4 [69].

Table 5.4: Comparison between alternatives to ITO, this work, and ITO bench mark based on Haacke's FoM.

Alternative	FoM (Ω^{-1})	Advantage	Disadvantage	Reference
Graphene	0.34×10^{-3}	High transparency	*Very high R_s *Requires high vacuum	[69]
Electrospinning	13.50×10^{-3}	*High transparency *Low R_s	*Nanostructure is very random *NW cannot be replaced *Process acidity	[33]
PEDOT:PSS	2.39×10^{-3}	Flexible	*Toxic *High acidity *Post treatment required.	[7]
NW field-assisted directed assembly	2.39×10^{-4}	*High throughput *Solution processed *Room temperature and pressure *Simple and low cost	*T reduced by assembly electrode size *Relatively high R_s	This work

The FoM bench mark is $35 \times 10^{-3} \Omega^{-1}$ for ITO with 90% light transmission, whereas the FoM of commercial ITO is $5 \times 10^{-3} \Omega^{-1}$ [71], which is higher than our approach by around an order of magnitude. This is mainly due to the high transparency; it should be noted that the light transmission in Haacke's FoM is raised to the tenth power, which greatly emphasizes its role in this FoM.

Contacts between NWs, with examples seen in Figure 5.11, cause high resistance, which has been reported to be much greater than NW resistance itself. Therefore, contact resistance has a major contribution to substrate conductance in general [65] and is an avenue to explore for future work. TEs by our approach allow the control of nanostructure, whereby repeatability of light transmission and sheet resistance results is obtained. Other approaches, such as electrospinning, feature very high transparency and sheet conductance; however, they show large randomness in the structure.

Chapter 6

Conclusions and Future Work

6.1 Conclusions

We produced nanostructured substrates for transparent electrode applications using field-directed chaining. Field-directed chains are initiated at the assembly electrode edges, where dielectrophoretic forces due to the gradient of the electric field dominate. In regions of low electric field gradient in between, but far from the electrodes, NW chains form by the effect of dipole-dipole interaction between the polarized NWs. The dipole-dipole interaction forces the connectivity between NWs during the assembly process. This process allows creation of ordered nanoscale patterns over a large area at a low cost and with potential for high throughput rate. Using this process, we obtained a high ratio of optical transmittance to sheet resistance without further post-processing. We found that the change of optical and electrical properties while varying the NW concentration in suspension is non-monotonic. This occurs due to the change in the nature of NW chaining. Based on experimental results that involved measurements and analysis of the optoelectronic properties of 27 substrates, our approach shows promise for achieving ITO replacement. Although the highest figure of merit (FoM) in this work, $2.4 \times 10^{-4} \Omega^{-1}$, has exceeded the FoM of another ITO-replacement, multilayer film-based transparent electrodes, there is room to enhance the FoM significantly, as it is an order of magnitude less than commercial ITO.

Using other approaches to deposit NWs on transparent substrates, such as drop-casting and spraying, results in random orientation of the NWs. In addition, these techniques require a high NW concentration to ensure the connectivity between NWs. These approaches require post processing to define the conductive nanoscale patterns.

These processes may involve selective etching or laser ablation. Such subtractive patterning results in NW loss, time consumption, and potential environmental pollution due to the toxicity of the dust of NWs. However, our methodology allows for nanoscale pattern control without subtractive patterning processes or using expensive tools, such as electron beam lithography. We showed that the patterns of NWs are uniform and with controlled orientation leading to better connectivity between NWs. Further, our technique allows several options for substrate NW material and geometry. Substrates are also reusable. Reusable substrates help in case the material has been degraded, which could affect its electrical properties. NW-chained TEs are distinctive, because they will not be completely opaque at very high concentrations since the NW chaining dam has been used during the chaining process. The NW chains are restricted to areas by a dam leaving parts of the substrate clear.

In this work, we showed the effects of the operating parameters on the optical and electrical properties of NW chaining-based TEs. We found that low NW concentration, typically below 0.8×10^8 NW/mL, do not show increase in electrical conductance due to very few chains formed. Moreover, the nature of NW chaining changes while varying the NW concentration. We found that the NWs gather near the assembly electrodes, creating clumps. This has led to a counter-intuitive behavior within a subrange of concentrations, in which sheet resistance and light transmittance both increase with increasing NW concentration in the suspension.

We found that the fraction of functional NW chains between two assembly electrodes can be increased by using high electric field strength for NW chaining. The fraction of functional NW chains was quantified using ImageJ software and used as a measure of the performance of chained-NW substrates. A high fraction of functional NW chains segment improves transparency and electrical conductance. The fraction of functional NW chains is influenced significantly by NW concentration and electric field strength.

6.2 Future Work

This work towards transparent electrode applications is relatively new, and lays the foundation for further substrate electrical and optical properties enhancement. Such enhancement can include new pattern design and NW-NW contact resistance reduction, by thermal or mechanical post-processing.

6.2.1 Hexagonal Array Nanostructure

During this work, a new design has been made to be fabricated on a transparent substrate. The design involves a pattern that produces nanowire chains in an array of a hexagonal shape. This will lead to a significant increase in light transmission since the assembly electrodes used are $30\text{-}\mu\text{m}$ dots connected by thinner busbars, rather than the $30\text{-}\mu\text{m}$ wide strip electrodes. This would reduce the metalized area occupied by the assembly electrodes, as seen in Figure 6.1. The ratio of covered area to the open area will decrease allowing for higher light transmission.

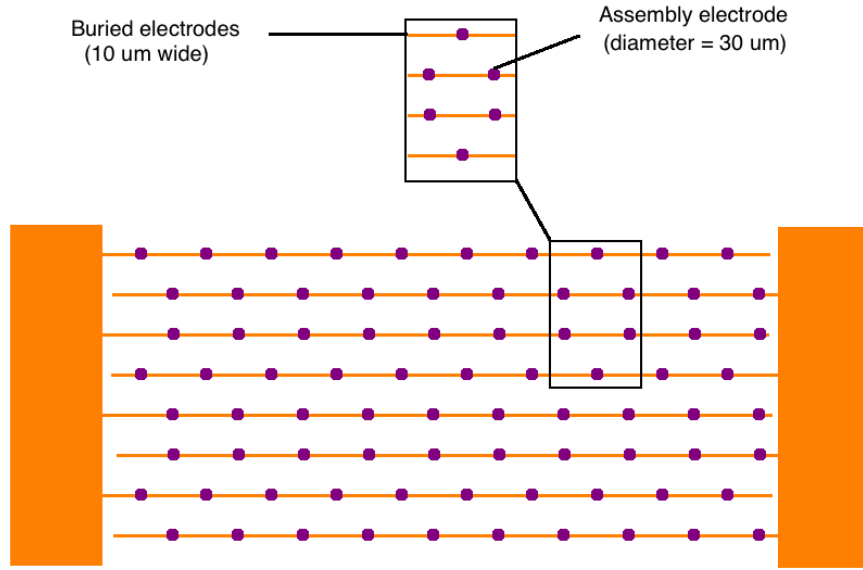


Figure 6.1: Micro-pattern substrate for hexagonal array nanostructure illustration.

The transparent area is larger in case of using the thin busbars that connect the circular assembly electrodes. This was concluded by comparing same enclosed areas in case of using the proposed design with the current interdigitated electrodes (see Appendix A.6 for further details). It is expected that the substrates with interdigitated busbars with gap size of 120 , 180 , and $240\mu\text{m}$ would have a light transparency of 86% , 89% and 94% , respectively.

Additionally, Layani et al. [20] presented the advantages of a honeycomb. Such a structure optimizes overall electrical sheet conductance while maintaining the high transparency of the substrate [20] since more parallel paths are introduced. Other approaches have obtained the honeycomb structure via self assembly and nanoimprint lithography [20][40].

6.2.2 Enhancing Sheet Resistance

Due to NW-NW contact resistance, reported to be much greater than NW resistance itself [65], NW network sheet resistance can be decreased further without manipulating NW concentration. Many approaches have been used for enhancing the overall sheet resistance. Madaria et al. [72] reported that a NW annealing process decreases the sheet resistance by a factor of 3.

Another approach, Joule heating involves passing a current through the chained NW network, sufficient to decrease NW contact resistance. This has been reported by both Song et al. [65], who applied steady electric current through NW network, and Leiterer et al. [73], who used voltage pulses to reduce sheet resistance. Welding the NWs by UV light exposure can also be used to improve sheet conductance [74], as well as plasmonic welding [75].

Appendix A

Additional Information

A.1 Resistance of NW Chain Patch between Assembly Electrodes

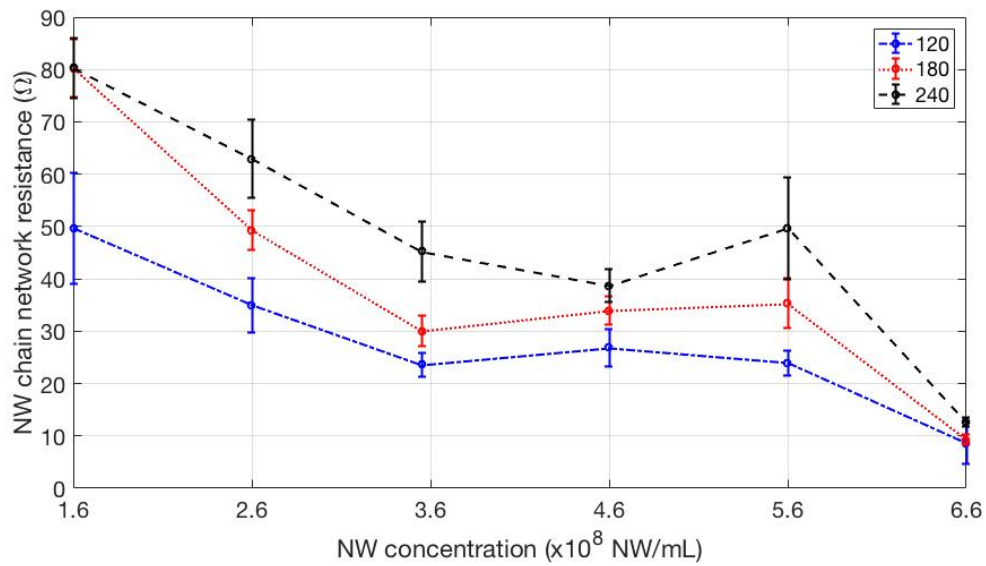


Figure A.1: R_{patch} for each NW concentration and substrate gap size including error margins which was applied in equation 4.6.

A.2 Functional and Nonfunctional NW Chains

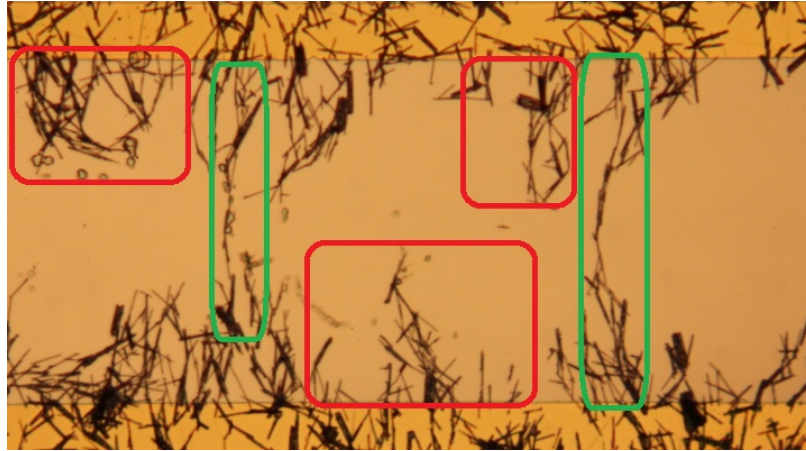


Figure A.2: NW chains between two assembly electrodes. The functional NW chains are marked with green. The nonfunctional NW chains marked with red.

A.3 NW Chaining with Fixed Electric Field

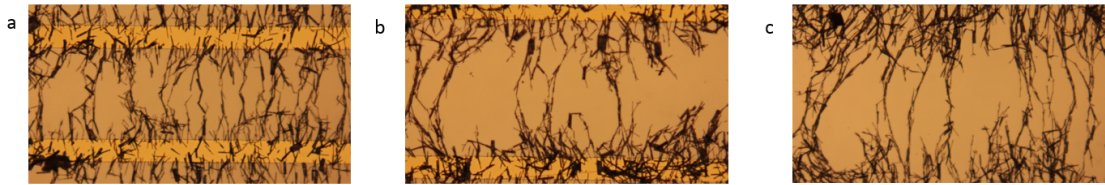


Figure A.3: NW concentration E chained on substrate a) $120\mu\text{m}$, b) $180\mu\text{m}$, and c) $240\mu\text{m}$ with a fixed electric field of 29.2 kV/m

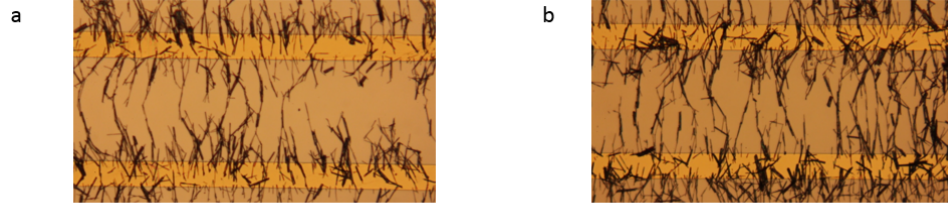


Figure A.4: 120 μ m substrate chained with NW concentration E, with electric field of a) 29.2 kV/m and b) 41.7 kV/m

A.4 Figure of Merit, Optical Transparency, and Sheet Resistance of Each Substrate

Measured light transmission, calculated sheet resistance and FoM of the NW chains-based transparent electrodes (this work). Tables A.1 and A.2 were referenced in Chapter 5 to show the details of the opto-electronic properties of our devices.

Table A.1: Light transmission, sheet resistance, and Haacke's figure of merit of each sample chained with fixed voltage, 5 V, i.e. varying electric field.

Gap size (μ m)	Substrate properties	NW Concentration ($\times 10^8$ NW/mL)					
		1.6	2.6	3.6	4.6	5.6	6.6
120	T (%)	66	65	65	67	61	59
	R_s (Ω /sq)	807.06	568.83	383.26	436.05	389.50	140.22
	FoM	1.94E-05	2.37E-05	3.51E-05	4.18E-05	1.83E-05	3.65E-05
180	T (%)	72	70	70	72	67	64
	R_s (Ω /sq)	868.60	534.26	325.64	367.34	382.77	100.67
	FoM	4.31E-05	5.29E-05	8.67E-05	1.02E-04	4.76E-05	1.15E-04
240	T (%)	74	75	75	76	75	69
	R_s (Ω /sq)	652.27	510.89	367.77	314.19	404.15	102.51
	FoM	7.55E-05	1.10E-04	1.53E-04	2.05E-04	1.39E-04	2.39E-04

Table A.2: Light transmission, sheet resistance, and Haacke's figure of merit of each sample chained with fixed electric field, 29.16 kv/m, i.e. varying applied voltage.

Gap size (μm)	Substrate properties	NW Concentration ($\times 10^8$ NW/mL)	
		2.6	4.6
120	T (%)	66	68
	R_s (Ω/sq)	830.12	710.79
	FoM	2.20E-05	2.97E-05
180	T (%)	73	75
	R_s (Ω/sq)	518.09	394.49
	FoM	8.30E-05	1.43E-04
240	T (%)	78	77
	R_s (Ω/sq)	483.67	314.95
	FoM	1.72E-04	2.33E-04

A.5 Haacke's FoM

Transmission (T) and sheet resistance (R_s) can be related directly to a figure of merit, F, the simplest form of which is:

$$F = \frac{T}{R_s} \quad (\text{A.1})$$

whereas transmission is expressed as follows:

$$T = e^{-\alpha t} \quad (\text{A.2})$$

where α is light absorption coefficient of the material, and t is the thickness. However, R_s can also be expressed as follows:

$$R_s = \frac{1}{\sigma t} \quad (\text{A.3})$$

where σ is the conductivity. Substituting equations A.2 and A.3 into A.1 gives:

$$F = \sigma t e^{-\alpha t} \quad (\text{A.4})$$

As a result, F is a function of material thickness. At what thickness will F be maximum? To find maximum transmissivity, T_{max} we set

$$\frac{dF}{dt} = 0 \quad (\text{A.5})$$

which yields $t = 1/\alpha$, for which

$$\frac{d^2 F}{dt^2} < 0 \quad (\text{A.6})$$

confirming this value of t maximizes F . Substituting in A.2 gives $T = 1/e = 0.37$, which can be interpreted to that $\max F$ occurs at transmittance of only 37%. Since the transparency of the benchmark (ITO) is 90%, we would like to define a FoM which has its maximum value at a transparency of 90%. Noting that $0.37^{0.1} = 0.90$, we can show that this has motivated the definition of Haacke's FoM as

$$F_{Haacke} = \frac{T^{10}}{R_s} \quad (\text{A.7})$$

satisfies this condition. The reader can repeat all the steps in the above derivation using the definition A.7 to confirm that the maximum value of F occurs at thickness $t = 1/10\alpha$, and the transmittance at this value of t is $T = 90\%$.

A.6 Effect of Changing Interdigitated Thick Bar Electrodes to Dot Electrodes on Light Transmission

Since transmission is ratio of open area to the total area ($T = \text{open area} / \text{total area}$), the expected light transmission of the pattern in Figure 6.1 without NW chains within Cary50 light beam dimensions that has an area of 0.8023 mm^2 would be as follows:

Table A.3: Expected light transmission of hexagonal array electrode pattern that governs the nanostructure

Gap size (μm)	Covered area due to honeycomb assembly electrode (mm^2)	Covered area due to buried interdigitated electrode (mm^2)	Total covered area (mm^2)	Transmission (%)
120	0.050868	0.06035	0.1112	86.13
180	0.022608	0.04430	0.0669	89.65
240	0.014836	0.03209	0.0469	94.15

Using assembly electrode in a circular shape connected with thin busbars reduces the area covered by the assembly electrodes that results in an increase in light transmission. For comparison, the current transmission percentages are 80, 85 and 88% for

the 120, 180 and 240 μm gap sizes, respectively.

A.7 Large Clumps of NWs That Contribute to Sheet Resistance Increase Due to R_c

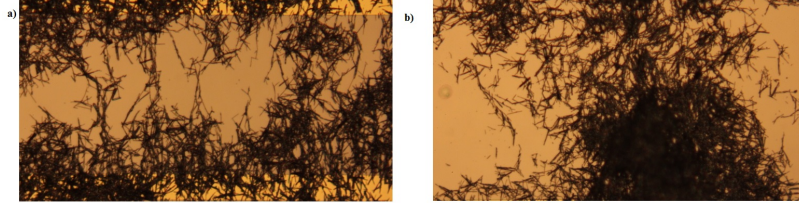


Figure A.5: a) 180 μm substrate and b) 240 μm substrate chained with NW concentration F. NW clumps between two electrodes increases R_c

A.8 Experimental Data and Theoretical Verification of Correction Factor

Experimentally, we have found the effects of gold bars that connect the NW-chains patch as discussed in section 4.4.1. Here, we show the raw data of NW chain patch before and after isolation in Table A.4.

Table A.4: Change in resistance before disconnection (R_1) and after disconnection (R_2)

Well No.	R_1 (Ω)	R_2 (Ω)	Change in R (R_2/R_1)
1	46.38	88.1	1.90
2	43.47	88.5	2.04
3	43.5	73.5	1.69
4	38.24	89.05	2.33
5	39.86	74.1	1.86
6	44.85	83.66	1.87
7	46.4	89.7	1.93
Average change			1.95

NW chain patches are connected in parallel, as in Figure A.6. Each patch is separated by resistance of the gold bar that is $\approx 0.1R_{patch}$. The equivalent resistance of the resistors number 1 and 2 is as follows:

$$R_{eq} = \frac{1}{1.2R_{patch}} + \frac{1}{R_{patch}} \quad (\text{A.8})$$

$R_{eq} = (1/1.83) = 0.54 R_{patch}$, which is close to the correction factor based on experiment, (1.95). In fact, this leads us to conclude that due to gold bar resistance, only two chains are being taken into accounts, while wasting the presence of all the remaining chains.

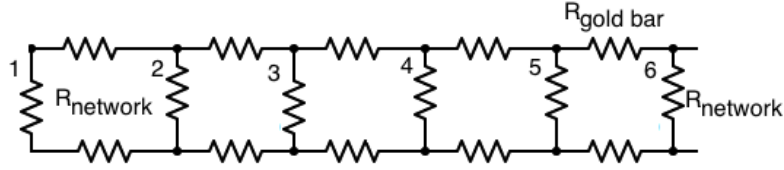


Figure A.6: Electrical equivalent circuit of NW chains and assembly electrodes

A.9 Photolithography and Lift-Off Process

The process to fabricate micron-patterned substrates via photolithography is as follows^[51]:

1. Mask design was created by using micron-scale design software, L-Edit, and written on shadow substrate.
2. 4" glass substrate was cleaned and spun coated with a positive photoresist with a thickness of 1 μm .
3. Later, the glass substrate, that contains photoresist, was exposed under shadow mask to UV light for 4 seconds.
4. Then, the sample was soaked in a developer for 55 seconds to solute the exposed part of the photoresist.
5. Following that, the sample was loaded into an e-beam evaporator (physical vapor deposition) to deposit gold.
6. Finally, soak the sample in Microposit remover to lift-off the unwanted material, for 24 hours in room temperature.

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