CUI, ZHENG. Silver nanowire-based flexible and stretchable devices: applications and manufacturing. (Under the direction of Dr. Yong Zhu).

The focus of this study is using silver nanowire (AgNW) as functional material to develop flexible and stretchable electronics for wearable applications. The applications of the wearable sensors towards touch-input and health monitoring are investigated. A novel AgNW patterning technique with Electrohydrodynamic (EHD) printing is developed to directly print functional AgNW patterns on a variety of substrates. In addition, temperature coefficient of the AgNW percolation network is studied and a highly stretchable wearable temperature sensor using kirigami structure is developed.

In recent years wearable devices have attracted significant attention. Flexibility and stretchability are required for comfortable wear of such devices. In this research, flexible and stretchable touch sensors with two different patterns (interdigitated and diamond-shaped capacitors) were developed. The touch sensors were made of screen-printed AgNWs electrodes embedded in polydimethylsiloxane. For each pattern, the simulation-based design was conducted to choose optimal dimensions for the highest touch sensitivity. The sensor performances were characterized as-fabricated and under deformation (e.g., bending and stretching). While the interdigitated touch sensors were easier to fabricate, the diamond-shaped ones showed higher touch sensitivity under as-fabricated, stretching or even bending conditions. For both types of sensors, the touch sensitivity remained nearly constant under stretching up to 15% strain, but varied under bending. They also showed robust performances under cyclic loading and against oxidation.

AgNWs-based conductor is a promising component for flexible and stretchable electronics. A wide range of flexible/stretchable devices using AgNW conductors has been demonstrated
recently. High-resolution, high-throughput printing of AgNWs remains a critical challenge. EHD printing has been developed as a promising technique to print different materials on a variety of substrates with high resolution. In this work, AgNW ink was developed for EHD printing. The printed features can be controlled by several parameters including AgNW concentration, ink viscosity, printing speed, stand-off distance, etc. With this method, AgNW patterns can be printed on a range of substrates, e.g. paper, polyethylene terephthalate (PET), glass, polydimethylsiloxane (PDMS), etc. First, AgNW samples on PDMS were characterized under bending and stretching. Then AgNW heaters and electrocardiogram (ECG) electrodes were fabricated to demonstrate the potential of this printing technique for AgNW-based flexible and stretchable devices.

Body temperature is an important indicator of health condition. It is of critical importance to develop smart temperature sensor for wearable application. A stretchable AgNW-based thermoresistive temperature sensor is developed. AgNW is half-embedded in a colorless polyimide film to improve the stability of the sensor. Temperature coefficient of resistance (TCR) of AgNW network is engineered by modifying nanowire density and applying different thermal annealing process. The temperature sensor is patterned with Kirigami structure, which enables stable resistance under large tensile strain (up to 100%). Demonstrated applications in monitoring the temperatures at biceps and knee using the stretchable temperature sensor illustrate the promising potential for wearable applications.
Silver Nanowire-based Flexible and Stretchable Devices: Applications and Manufacturing

by
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DEDICATION

To my parents, Hongdan Nie and Zhenshan Cui.

To the special girl, Jiayi Ruan.
BIOGRAPHY

Zheng Cui received his B.S. degree in Process Equipment and Control Engineering from Hefei University of Technology, Anhui, China, in 2013. He joined the Dr. Yong Zhu’s group (Nanomechanics and Nanoengineering Laboratory) and had since pursuing his Ph.D. degree in Mechanical engineering. His research interests include synthesis, nanomechanics and fundamental properties of nanowires, as well as advanced fabrication techniques of nanomaterial-based flexible and wearable electronics.
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Chapter 1

Introduction

1.1. Development of Flexible and Stretchable Devices

Flexible and stretchable electronics, emerging technologies in the last decades, have garnered significant attention from industry and academia. Flexible electronics is a technology that apply functional materials onto bendable substrates (e.g., plastic sheet) and achieve various applications. A variety of novel applications has been enabled, including flexible circuits,\(^1\) flexible displays,\(^2\) flexible solar cells,\(^3\) electronic paper,\(^4\) flexible touch screens,\(^5\) implantable medical devices\(^6\) and robotic systems with sensory skin.\(^7-8\) However, with the development and increasing need of wearable devices, flexible devices cannot fulfill the requirement of wearable applications, which the electronics must not only bend but also survive large deformation (e.g., stretching, compressing and twisting) and deform into complex, curvilinear shapes. Hence, stretchable electronics are developed to meet the wearables’ requirement by implementing functional material on the surface of stretchable substrate or by embedding in a stretchable matrix.

Stretchable devices can be achieved by building new structures with conventional materials, using new materials in conventional fashion or combing the two strategies. Conventional materials (e.g. inorganic semiconductor) in the format of thin film has been well developed in the application of stretchable electronics, owing to such flexible film can accommodate large strain with introduced wavy structures. With recent advance in development of nanomaterials, highly stretchable electronics can be achieved by depositing the functional nanomaterials on the surface of stretchable substrates or partially/completely embedded in a stretchable matrix. According to the geometry, nanomaterials can be categorized into 0D materials (e.g., nanoparticles), 1D materials (e.g., CNTs, nanowires) and 2D materials (e.g., graphene).
Though stretchable devices are developed based on 0D materials, but their performance is limited mainly due to the low aspect ratio of the materials.\textsuperscript{9-10} 1D materials with high aspect ratio can effectively form conductive network in/on the stretchable substrates and have shown promising progress in development of stretchable devices. Graphene as the predominant 2D material has been widely developed in application of transparent conductors. Graphene monolayer with excellent transmittance and high conductivity has the potential to replace indium tin oxide (ITO), which is widely used in commercial electronics. A comprehensive review of nanomaterials and their application is presented in the following chapter.

Techniques of fabricating flexible and stretchable electronics with inorganic materials can be categorized in top-down and bottom-up approaches. The most widely used top-down fabrication technique is photolithography, which provides high resolution (down to several nanometers), excellent repeatability and large scale of patterning functional materials. Followed by transfer techniques and selective bonding, the high precision 2D functional patterns are transferred to stretchable substrates (prestrained or non-prestrained). The introduced strain (stretching and releasing) initiates the 2D patterns deforms to 3D structures with negligible local strain in the functional materials. A wide variety of stretchable electronics with high performance has been developed, even with non-stretchable inorganic materials.

Bottom-up, a complementary approach to top-down, includes directly growing (or followed by transfer process), depositing and printing of functional nanomaterials on targeting substrates. Printing techniques are the predominant approach in developing electronics with complicated designs and they can be scaled up to roll-to-roll fabrication for industry applications. Nanomaterials patterned with printing techniques can achieve unique performance with special design of the printed traces (e.g., serpentine patterns, fractal patterns). Categorized by their
working mechanism, printing techniques can be divided in contact printing and non-contact printing. Main printing techniques of 1D nanomaterials is introduced in the following chapter.

1.2. Nanomaterials Used for Flexible and Stretchable Devices

1.2.1. Carbon Nanotubes

CNTs are high aspect ratio 1-D molecule-scale tubes of graphite carbon with outstanding properties, including high mechanical strength, Young’s modulus, thermal conductivity, and electrical conductivity. Various synthesis approaches of CNTs are arc discharge, laser ablation, and chemical vapor deposition (CVD). CVD approach is the most widely used method for CNTs synthesis, able to grow CNT films either randomly distributed or aligned. Aligned CNT films can be fabricated using patterned catalysts, electric or magnetic fields during the CVD process, directional gas flow, or use of a substrate with defined lattice structure. However, devices with aligned CNT films components have poor statistical reproducibility, which will not be discussed here. In contrast with aligned CNTs, films with random distributed CNTs are more reproducible and are more practical for applications. Due to the high aspect ratio of CNTs, they are subject to large Van der Waals forces, which cause them to stick together, forming large clusters. Hence, dispersion of CNTs for solution-based deposition is challenging.

CNT/polymer composites are fabricated by dispersing CNTs into a polymer matrix. The superior properties (mechanical, electrical and optical properties) of CNTs make them as promising filler materials to form composites. Single walled CNTs (SWCNTs) are uniformly dispersed in fluorinated copolymer with jet-milling process to make stretchable conductors. The as-fabricated composite can be stretched by 118% with a constant conductivity of 9.7 S cm⁻¹ (of 1.4 wt% SWCNTs) or by 29% with a constant conductivity of 102 S cm⁻¹ (for 15.8 wt% of
SWNTs). Increasing the mass fraction of the CNTs improves the conductivity, but limits the stretchability of the stretchable film. Adding other conductive nanomaterials or doping CNTs further improve the conductivity of such conductive composites. Micro-sized silver flakes and multi walled CNTs (MWCNTs) were mixed in a fluorinated copolymer as ink for drop casting. Perforating and embedding into a nitrile butadiene rubber (NBR) substrate compensated the limited stretchability of the composite caused by introduced silver flakes and MWCNTs. The added silver flake bridged more electrical pathways in the composite, dramatically improved the conductivity to 5710 S cm\(^{-1}\) at 0\% strain and 20 S cm\(^{-1}\) at 140\% strain.\(^{27}\) P-type doping through acid treatment provides an alternative way to enhance the conductivity of the composites without sacrifice it’s stretchability.\(^{28-29}\) Kim et al. reported spray coating approach to fabricate highly stretchable SWNT-ionic-liquid/silicone-rubber composite with relative low SWCNTs content of less than 4\%. After nitric acid treatment, the as-fabricated electrode can be stretched to 200\% with a constant conductance of 18 S cm\(^{-1}\) after 20 loading/unloading cycles.\(^{30}\) Back filling porous CNTs structure with elastomer enables its robust behavior under stretching, bending and twisting. The original conductivity of the SWCNT-aerogel-Polydimethylsiloxane (PDMS) composite is 0.83 S cm\(^{-1}\). By changing the volume fraction of SWCNT, the composite can become highly transparent (T = 93\%) with original conductivity of 1.08 S cm\(^{-1}\). Both of the SWCNT-aerogel-PDMS composites showed stable resistance after 5 cycles of loading/unloading to 100\% tensile strain.\(^{31}\) Additional approaches in fabrication of conductive and transparent CNTs-based stretchable conductors are spray coating and Meyer rod coating of CNTs on transparent substrates. Doped SWCNTs that spray-coated on pre-strained PDMS shows 328 Ω sq\(^{-1}\) at transmittance of 79\%, which is stabilized within 50\% strain.\(^{32}\) Polymer light-emitting electrochemical cells (PLECs) are fabricated by Meyer rod coating of CNT on PtBA substrate. The electrode has a sheet resistance
of 500 Ω sq⁻¹ and transmittance of 87%. In addition to the CNTs-based conductors that show relative stable resistance behaviors under tensile strain, other CNTs-based conductors that able to accommodate large tensile strain (up to 700%) are also developed, indicating excellent stretchability of CNTs.

![Figure 1.1](image)

**Figure 1.1** (a) SEM images of CNT/copolymer campsite. Finer or exfoliated bundles of SWCNTs were uniformly dispersed in rubber and formed well-developed conducting networks. (b) SEM image. Silver flakes and MWCNTs are uniformly distributed in polymer matrix to enhance the conductivity. (c & d) Nitric acid enhanced the conductivity of low SWCNT content film. The conductor showed stable resistance under 200% strain after 20 cycles of loading and unloading.
1.2.2. Graphene-based Materials

Graphene-based materials are attractive candidates for applications in flexible and stretchable electronics owing to its excellent mechanical, electrical and optical properties. Additionally, as a 2D structured material, graphene-based electronics can be easily manufactured and scaled up by conventional fabrication techniques. Large area and high quality of graphene sheet can be synthesized by CVD method on metal films using a gaseous carbon source. Commonly used metals are Ni, Fe, Co, Pt and Cu, which serves as catalyst and substrate in the synthesis of graphene films. Metals with higher solubility of carbon atoms are able to produce thick graphene films (e.g., Ni, Fe and Co). While metals with lower solubility are good for generating graphene monolayer. Conventional CVD need a high processing temperature (~1000 °C), which make it challenging to direct growth graphene on plastic substrates. Plasma-enhanced CVD (PECVD) enables synthesis of graphene sheets at low processing temperature (~300 °C), but the properties of the grown graphene are inferior to that synthesized by conventional CVD method. Hence, to achieve high quality graphene sheet without defect generation and quality
degradation, transfer techniques are commonly used. For instance, the most effective transfer technique is a solution-based technique with the assist of poly(methyl methacrylate) (PMMA) or PDMS. As the transfer process can be adjusted to roll-to-roll fabrication, potential industrial applicable approach of manufacturing larger area of graphene film has been developed. Bae et al., achieved 30 inches of graphene with exciting optoelectrical properties. The as-prepared graphene monolayer has a high transmittance of 97.4% at 500 nm and reasonable sheet resistance of 125 Ω sq$^{-1}$. Additionally, the transparent electrode can survive 6% tensile strain with almost no resistance change. Three-dimensional flexible and stretchable interconnected graphene network is realized by conducting direct CVD synthesis of graphene on Ni foam. After removing Ni and PMMA sacrifice material, the graphene foam achieved is highly conductive (10 S cm$^{-1}$) with low graphene flakes loading of ~0.5 wt%.$^{42}$ A resistive strain sensor was developed based on the graphene foam and achieved gauge factor of ca. 2 at maximum strain (~95%).
Figure 1.3 (a) Schematic of the roll-to-roll production of graphene films grown on a copper foil. The process include adhesion of polymer supports, copper etching (rinsing) and dry transfer-printing on a target substrate. A wet-chemical doping can be carried out using a similar setup to etching process. (b) A transparent ultra large-area graphene film transferred on a 35-inch PET sheet. (c) An assembled graphene/PET touch panel showing outstanding flexibility. (d) UV-vis spectra of roll-to-roll layer-by-layer transferred graphene films on quartz substrate. (e) SEM image of a CVD synthesized graphene foam.
Graphene flakes can be obtained by chemical exfoliation (CE) approach from graphite in liquid environments. However, the obtained graphene oxide (GO) is not electrically conductive and reduction treatment is required to recover its original conductivity (rGO). For instance, chemical reduction by hydrazine and thermal reduction (\(~300 \, ^\circ\text{C}\)) in an inert atmosphere.\(^{43-44}\) Moreover, low temperature and low atmospheric pressure reduction process is realized by plasma-assisted reduction. And this technique can be integrated with existing roll-to-roll fabrication to achieve large area rGO films. Similar to metallic nanomaterials, graphene flakes can be dispersed in solvent for printing.

Graphene-based ink was obtained by liquid phase exfoliation of graphite in N-methylpyrrolidone and printed into transparent and conductive patterns by ink jet printing. The printed patterns have a transmittance of \(~80\%\) and sheet resistance of \(~30 \, \text{k}\Omega \, \text{sq}^{-1}\). A thin film transistor was also developed with mobilities up to \(~95 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}\).\(^{45}\) Eda et al., developed a solution-based method that allows uniform and controllable deposition of rGO thin films over large area. By varying the concentration of the GO in solution or the filtration volume, the thickness of the obtained GO films ranges from single monolayer to several layers. After the obtained GO films reduced by dimethylhydrazine vapor and annealed at \(200 \, ^\circ\text{C}\) in nitrogen atmosphere. The rGO films have a sheet resistance of \(10^5\) at \(T = 98\%\) and \(43 \times 10^3\) at \(T = 60\%\).\(^{46}\) Moreover, Pham et al., developed a scalable rGO deposition method through supersonic kinetic spray coating. The prepared rGO films had a low sheet resistance of \(2.2 \times 10^3 \, \Omega \, \text{sq}^{-1}\) and a high transmittance of \(T = 84\%\) at wavelength of 550 nm.\(^{47}\) By mixing crumbled graphene and nanocellulose in PDMS substrate, a resistive strain sensor with high gauge factor (7 at 100%) was developed for a smart gloves to detect finger movement.\(^{48}\)
Figure 1.4 (a) Optical image of highly transparent, uniform and flexible rGO electrode over larger area on plastic substrate. (b) Transmittance at 550 nm as a function of filtration volume for reduced GO thin film. (c) Sheet resistance as a function of filtration volume for reduced GO thin film.\textsuperscript{46} (d) Top view of the stretchable nanopaper with fully embedded structure. (e) Photograph of the data glove with five implanted sensors. The bending and stretching states of the glove finger during testing are also shown. Scale bar: 2 cm. (f) Relative resistance change for the five independent strain sensors.\textsuperscript{48}
1.2.3. Metallic Nanomaterials

Metallic nanomaterials including metallic nanoparticles (NPs) and metallic nanowires (NWs) have received much attention in the application of flexible and stretchable electronics owing to their high electrical conductivity. Compared with NPs, high aspect ratio of NWs enables its application when large deformation is involved.

Silver nanowires (AgNWs), as one of the most conductive materials, have become the most extensively studied metal nanowire as conductors. Silver nanowire can be synthesized by a variety of methods, including hydrothermal method, microwave-assisted process, electrochemical technique, UV irradiation technique, template technique. In comparison with these methods, the polyol synthesis process appears the most promising synthetic procedure in the aspect of easy mass production, low cost and simplicity. Note that this is a solution-based synthetic process, the as-synthesized AgNW can be directly adapted to the following solution-based conductor fabrication process seamlessly. AgNWs that synthesized by polyol method typically have a diameter of 30 - 200 nm and a length of 1-20 μm. Theoretically, nanowires with larger diameter and longer length are more conductive than the nanowires with smaller diameter and shorter length. Lee et al. developed a successive multistep growth (SMG) method to effectively increase the size of synthesized nanowires. The average length and diameter of the synthesized nanowires after seven repeated steps are reported to be 96.1 μm and 160 nm, respectively.

AgNW-based transparent electrodes have been extensively studied as a substitute to indium tin oxide (ITO has excellent optoelectronic properties with a sheet resistance on the order of 10 Ω sq\(^{-1}\) at about 90% optical transparency). De et al. developed a conductor with optical transmittance of T = 85% and sheet resistance of Rs = 13 Ω sq\(^{-1}\) on PET substrate by vacuum
Figure 1.5 (a) Uniformly distributed AgNW on substrate surface to form highly conductive and transparent conductors.\textsuperscript{55} (b) SEM image of GO-soldered AgNW junctions (indicated by red arrows).\textsuperscript{67} (c) TEM image of NW-NW junction after plasmonic welding. Scale bar is 50 nm.\textsuperscript{68} (d) Micro-wavy structures generated in the AgNW/PDMS enables stable conductivity with strain of 0-50\%.\textsuperscript{71} (e) Very long AgNW-based conductors showed excellent stretchability and conductivity over short AgNW.\textsuperscript{50} (f) Size comparison of very long AgNW synthesized by SMG process with AgNW grown by conventional method.\textsuperscript{51}
sq$^{-1}$ and 80% diffusive transmittance in visible range by Meyer rod coating. Leem et al. spin-coated AgNW on glass substrate and achieved Rs = 35 $\Omega$ sq$^{-1}$ at 98% transmittance. By using spray coating approach, Scardaci et al. achieved AgNW network with Rs = 50 $\Omega$ sq$^{-1}$ and T = 90% over large area of PET substrate. AgNWs coated on PET substrate showed superior optoelectronics properties and excellent flexibility under bending. Hence, a wide range of AgNWs-based flexible device are developed, including OLEDs, shape-memory polymer LEDs and solar cells.

AgNWs-based stretchable conductors are also demonstrated recently. General approaches in fabricating such devices are depositing NWs on the surface of the elastomer, embedding NWs in the middle of elastomer or just below the surface of the elastomer, and uniformly mixed with elastomer. The adhesion between nanowires and substrate is of importance, especially for surface coated application. Akter et al. used polydopamine to adjust the surface property of PDMS substrate from hydrophobic to hydrophilic, in order to improve the uniform distribution of AgNW on the substrate and enhance the interface adhesion between AgNW and substrate. The spray-deposited AgNWs conductor showed a low Rs = 35 $\Omega$ sq$^{-1}$ at T = 80% and good robustness against strain below 15% tensile strain. Pei et al. embedded AgNWs just below the surface of a series stretchable substrates, including poly(acrylate), PU, and poly (tert-butyl acrylate) (PtBA). Acrylic acid (AA) is used for enhancing the adhesion between AgNW and polymers in the case of poly(acrylate) and PtBA. It helped the transfer of the AgNWs into the polymer matrix and ensured uniform AgNW percolation network deformation under loading. Sheet resistances of 50.8 $\Omega$ sq$^{-1}$ at T = 90.2% and 7.5 $\Omega$ sq$^{-1}$ at T = 79.6% were achieved in the AgNW-poly(acrylate) electrodes, and the sheet resistance increased by 2.3 times at 50% strain. A sheet resistance of 10 $\Omega$ sq$^{-1}$ was achieved by the AgNW-PtBA composite, and it remained conductive with a resistance of $10^2$-$10^3$
Ω sq⁻¹ when applied 140% tensile strain. The conductivity of the AgNWs-based conductor can be further improved by decreasing the contact resistance at the NW-NW junctions. Liang et al. used graphene oxide (GO) to solder the AgNW junctions, which greatly reduced the contact resistance, meanwhile enhanced the stretchability and stability of AgNW network. The as-fabricated conductor demonstrated a Rs = 26 Ω sq⁻¹ at T = 86.3% or Rs = 14 Ω sq⁻¹ at T = 82.5%. The sheet resistance was increased by 10.6 times under 80% tensile strain. Alternatively, treatment of AgNW junctions by plasmonic welding, thermal annealing and chemical treatment can also improve the conductivity. Garnett et al. used plasmonic welding to initiate a resistance drop of more than three orders and achieved conductors with Rs = 580 Ω sq⁻¹ at T = 95%. Lee et al. used very long AgNWs synthesized by SMG method to fabricate highly transparent and conductive conductors. The AgNWs film went through thermal annealing process and achieved low Rs = 9 - 70 Ω sq⁻¹ and T = 90 – 96%, and still highly conductive under strain up to 460%. NaCl treatment was also used to weld the AgNW junctions and the conductors achieved superior Rs = 5 Ω sq⁻¹ and T = 92%. Ho et al. developed a biaxially stretchable conductors by transferring AgNW network on pre-strained substrate. The conductors showed a Rs = 14 ± 2 Ω sq⁻¹ with T = ~85%, but it’s stable resistance range is only 5%. Though AgNWs-based conductors have excellent conductivity, most of them suffer from increasing resistance with applied strain or only stable resistance in a small strain range (e.g. <20%), which limits their applications as stretchable conductors. Xu et al. demonstrated a promising approach by embedding AgNW just below the surface of PDMS. The resistance became stable after first several loading/unloading cycles to 80% and then the conductor has a constant conductivity of 5285 S cm⁻¹ in a large range of applied strain (0 – 50%). Choi et al. enabled uniform mixing of AgNWs and polymers by conducting ligand exchange of
the AgNW surface. The reported conductivity of the AgNWs/polymer composite is \( \sim 7000 \text{ S cm}^{-1} \) and stable within 30\% tensile strain.\(^{71}\)

1.3. Manufacturing Mechanism for Stretchable Devices

Stretchable devices are achieved by engineering the structure of functional materials and intrinsic stretchable elastic substrates. Various methods have been used to develop stretchable devices. Intrinsic stretchable composites are used, but they often suffer high electrical resistivity. Smart structures pave another way to accommodate large deformation even with traditional silicon-based materials, involving wavy structures, fractal design, island-interconnect design, origami and Kirigami structure.

1.3.1. Intrinsic Stretchable Composites

In general, intrinsic stretchable composites are achieved by dispersing functional materials into elastomer substrates. Hence, the composites share the electrical properties from the rigid fillers and mechanical properties from soft matrix. Stretchable elastomers that widely used as substrate material includes natural rubber (NR), styrene butadiene rubber (SBR), polyurethane (PU), thermoplastic polyurethane (TPU), Ecoflex, and predominant poly(dimethylsiloxane) (PDMS), which have the merit of high stretchability (up to 1000 \% strain), low Young’s moduli (low as 55 kPa) and electrical insulation.

The ratio between the functional filler and elastomer need to be carefully engineered as it rises a tradeoff between electrical performance and mechanical stretchability. High loading of the functional material improves the conductivity, but also increase the stiffness and deteriorate the stretchability of the composite.\(^{26,30,72}\) Functional materials with high aspect ratio are preferred to
be used as filler material, mainly due to it can effectively build conductive network within the polymer matrix. In addition, the fillers need to be uniformly distributed in the elastomer to achieve homogenous electrical properties and mechanical properties.\textsuperscript{73-74} To improve the filler distribution, addition of surfactants and selection of suitable processing method are required.\textsuperscript{71} Composite properties such as uniformity and density can be engineered by dispersion techniques (e.g. ultrasonication,\textsuperscript{30, 74} jet-milling,\textsuperscript{26} and shear mixing\textsuperscript{75-76}) or exfoliation agents (e.g. ionic liquids\textsuperscript{27, 35, 77}). Besides random distribute the fillers in the polymer matrix, the functional material can also be deposited as a film and partially embedded in the surface of the elastomer to build stretchable electronics.\textsuperscript{48, 70}

Though the functional material/polymer composites can be stretchable and conductive, but the electrical performance is not stable over large strain, especially for the nanomaterial with low aspect ratio (e.g. nanoparticles, nanorods), where the contact between the fillers are losing under large strain. Hence, stretchable electronics with smart designs/structures are emerging to achieve stable performance over larger strain.

1.3.2. Wavy Structures

Inorganic semiconductor material has been widely used in conventional electronics, due to the brittleness of such material (fracture at strains of the order of 1%), such materials need to be engineered to smart structure to accommodate large strain. Mechanical buckling method has been demonstrated to be a promising approach to achieve ‘wavy’ structural configuration on the surface of elastomeric substrates, making stiff, brittle, thin-film layer flexible and stretchable. A key point in this strategy is that the brittle functional films need to be extremely thin (thickness $h \sim 100$ nm). With such thickness, the brittle films become very flexible to out-of-plane deformation as their
bending stiffness (proportional to $h^3$) and bending strain (proportional to $h$) both scale down with their thickness. The mechanism of mechanical buckling method includes (1) prestraining the elastomeric substrate, (2) depositing or transferring functional material/film onto prestrained substrates, (3) release the prestrained substrate to initiate the spontaneous out-of-plane buckling of the functional material.\textsuperscript{78} To control the periodic wavy structure on the elastomeric substrate, the thin film can be selectively bonded to a chemically patterned substrates.\textsuperscript{79}

Prestraining the elastomeric substrates is a crucial step to generate wavy structures. However, this step cannot be simply adapted to the existing industrial manufacturing process where prestrain is impossible/difficult, limiting its applications from large-scale manufacturing. Hence, new approaches without prestrain step is highly demanded. A new buckling method with prestrain step is developed recently, where the interface between the functional material and substrate plays an important role to form buckled structure. After the functional material is deposited/coated on the elastomeric substrate, a tensile stretching step is introduced to the substrate. The deposited/coated material slides on the substrate when stretching and buckled under releasing. After several stretching and releasing cycles, the stable buckled structure is formed and the resistance of the film become stable under stretching.\textsuperscript{34,80} Interestingly, such method can also be applied to nanomaterial films that embedded right below the surface of elastomeric substrate. Feng et al., found microscale wavy structures can also be generated when the AgNW/PDMS composite undergo stretching and releasing process after fabrication, mainly due to the property mismatch between the AgNW/PDMS layer and the whole PDMS substrate.\textsuperscript{70}
Figure 1.6 (a) Schematic illustration of the process for fabricating buckled wavy single-crystal silicon ribbons on a PDMS substrate. (b) Schematic illustration of the process for fabricating controlled wavy structure on PDMS with periodic activated and inactivated patterns. (c) SEM image of buckled GaAs nanoribbons. Inset: GaAs/PDMS substrate interface. (d) Schematic showing the deformation of AgNW/PDMS layer during the stretching and releasing process. The corresponding applied strain is indicated on the right.
1.3.3. Island-interconnect Design

Another effective strategy to build stretchable electronics is utilizing island-interconnect design and mesh structure to improve the overall stretchability of the functional devices. In this structural configuration, the functional island is the rigid part that chemically bonded to the stretchable substrate and the interconnects between the islands act as flexible bridges to accommodate larger strain applied. The stretchable interconnect plays an important role in this design and it could be engineered to extend the stretchability of the island-interconnect configuration. These interconnects could be prepared by low-temperature liquid metal\textsuperscript{81-82} or smart structures that could use out-of-plane deformation to mitigate the local strain (e.g. buckled ribbon and serpentine-shaped interconnects).\textsuperscript{83-84} The island-interconnect design can also be used to build conformal curvilinear electronics, which shows potential of such techniques in wearable applications.\textsuperscript{85} In general, the island-interconnect design demands long interconnects to achieve high stretchability, limiting its application when high areal coverage is required (e.g. solar panel). Hence, an advanced approach is proposed by mounting the island-interconnect structure onto a trenched elastomer, where the interconnects are buckled downward into the separating trenches.\textsuperscript{86}

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\caption{(a) Optical images of stretching tests of the island-interconnects design in x- and y-direction.\textsuperscript{85} (b) Schematic illustration of the steps for using silicon membrane circuits in mesh layouts and elastomeric transfer elements to wrap electronics onto substrates with complex curvilinear shapes, such as the dimpled surface of the gold ball shown here.\textsuperscript{86}}
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1.3.4. Fractal Design

Fractal patterns are defined as self-similarity: repeating itself at different scales. With different shapes of repeating patterns, the fractal patterns can have different mechanical behaviors to meet various electronics design requirement. By carefully engineering the shape of fractal patterns, they can be used to accommodate large strain in one selected dimension and to support biaxial, radial, and more complex deformation modes. Fan et al., presented six representative examples of fractal patterns and found Peano curve pattern is able to accommodate 75% uniaxial strain with local strain as low as 0.3%, paving the way to use conventional brittle materials in stretchable electronics.\textsuperscript{87}

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**Figure 1.8** (a) Six different patterns of metal wires fully bonded to EcoFlex substrates demonstrate the application of fractal designs as general layouts for stretchable electronics. (b) FEM images of each structure under elastic tensile strain and (c) their corresponding experimental MicroXCT images demonstrate their elastic mechanics. Scale bar, 2 mm.\textsuperscript{88}
1.3.5. Origami and Kirigami

Origami is an ancient art of paper folding, which is able to create three-dimensional structure from two-dimensional sheet through folding at designed creases. By carefully engineering the folding patterns, the designed origami structure can fit the requirement of foldable electronics, which is a key component for stretchable electronics. Moreover, the mechanical behavior of the folded structure can be very different to original 2D sheet. For instance, a Miura-ori structured aluminum foil can support weight more than 5 times of a flat aluminum foil sheet (16 glass slides to 4 glass slides), which is ~44 times of its own weight. And because of that, the deformed origami structure loses its flexibility. Besides, smart design or material are needed to accommodate the large bending strain at creases. Tang et al., developed a origami-enabled silicon solar cells which can reach up to 644% areal compactness while maintaining reasonable good performance upon cyclic folding and unfolding.

Kirigami is a variation of origami, in which cutting is included. Kirigami has the potential to transform rigid or even non-stretchable material into highly stretchable structure while releasing local strain by out-of-plane deformation, resulting in a remarkable electrical performance under large strain. By engineering the slit size, slit number and film thickness, ultra-stretchable electronics can be developed to survive large strain up to 840%. In addition, biaxial stretchable can be achieved by designing the open cuts. Compared with origami, the mechanical properties of kirigami structure does not change under deformation. Hence, the kirigami structure can be stretched in in-plane direction and be bendable in out-of-plane direction. A wearable heater inspired by kirigami pattern is developed, which is able to be stretched (maintaining stable heating performance) and wrapped around curvilinear body part (e.g. wrist joint).
Figure 1.9 (a) Miura folding enables stretchability. (b) Optical image of the fabricated origami-enabled Si solar cells at unfolded state. The inset show the metal trace embedded Parylene-C interconnects in serpentine shape. (c) Photograph of kirigami pattern before and after stretching. (d) Photographs of a fabricated parylene film placed over a beating mouse heart. (e) schematic of biaxial kirigami film before and after stretching. (f) IR image of a powered kirigami-inspired stretchable heater attached to wrist joint.
1.4. Techniques for Printing 1D Nanomaterials

The fabrication process of the devices needs to be facile, reliable, and scalable to large area. A number of technologies have been developed to apply solution-based 1-D functional nanomaterials on various flexible and stretchable substrates. According to the type of processing, the techniques can be divided into two types: deposition and patterning. The deposition methods including drop-casting, spin-coating, Meyer-rod coating, dip coating, spray coating, etc. These methods are good from small scale to large scale coating, but not suitable for high resolution patterning, and will not be discussed here. Recent patterning methods of 1D functional nanomaterial can be mainly categorized into contact printing and non-contact printing. In contact printing process, the patterned structures with inked surfaces need to have physical contact with the receiving substrate. In non-contact printing process, the nanomaterial ink is deposited through nozzle or opening, and the desired patterns are printed by the relative motion between the nozzle/opening and receiving substrate as programmed. Non-contact printing of 1D nanomaterials brings challenges in ink formation as the nanomaterials need to be uniformly dispersed. Otherwise, nozzle clogging during printing will decrease printing efficiency of such techniques. All the patterning techniques discussed here are suitable for lab-scale fabrication. And most of them can be adjusted to roll-to-roll (R2R) fabrication to realize fast and efficient mass manufacturing.

1.4.1. Contact Printing Techniques

The widely used contact-based printing techniques includes gravure printing, flexographic printing, micro-contact printing, in which the functional ink need to have physical contact to receiving substrates to initiate printing.
1.4.1.1. Gravure Printing

Gravure printing utilizes direct transfer of functional inks through physical contact of the patterned structure with the substrate. This technique can be adjusted to cost-effective R2R fabrication process to produce high quality patterns. A typical gravure printer consists of a cylinder roll, doctor blade, ink reservoir and substrate. The cylinder roll is usually electroplated with copper and engraved with micro cells which are processed with electromechanical methods or laser engraving. 93-94 The ink reservoir applies enough ink in the engraved cells and the doctor blade is used to remove the extra ink on the cylinder surface to ensure high resolution printing. To reduce the wear of engraved cylinder from ink transferring and contacting with substrate, the cylinder is usually coated with chrome for protection. 95 Even though, the engraved cylinder wears over time. Hence, a gravure-offset printing is developed by introducing one extra elastic blanket cylinder. 96 The width and the thickness of the printed patterns depends on the cell emptying, ink spreading behavior, dimensions of the engraving cell in the mold, print speed, ink viscosity and the ink/substrate surface energies. 97-99 Uniform lines can be printed by merging droplets at a cell spacing to cell ratio of 1.06 up to 1.40. When the ratio is greater than 1.40, printed line will be scalloped. 99 Additionally, gravure printing is challenging in printing small scale patterns in different directions. Experiments have shown magnifying dependence of the transferred ink on the angle between patterned-line direction and printing direction. 100 When the line width is very small, the ink transfer is limited if the patterned line direction is perpendicular to the printing direction. Researchers have developed R2R gravure printing systems that could direct print single-walled carbon nanotubes (SWCNTs) as active layer in large arrays of TFTs. 95, 101-102 Silver nanowires (AgNWs) are also printed by gravure printing. Park et al. printed transparent AgNWs line with smallest width of ~230 μm with a gravure trench width of 500 μm at speed of 12 cm/s. They also
developed AgNWs with 450 μm line width that showed resistivity of 320 Ω cm-1 with transmittance of ~95%.103

1.4.1.2. Flexographic Printing

Flexographic printing realized high speed and high-resolution printing over gravure printing.93 A flexographic printing systems including fountain roller, anilox roller, printing plate cylinder, impression cylinder, doctor blade, ink reservoir and substrate as shown in Figure 1b. The printing plate cylinder is covered with a rubber or polymer plate that is patterned with photolithography. Anilox roll determines the quality of ink being transferred to the printing plate and to the receiving substrate subsequently. The functional ink should not have high viscosity, otherwise it will result in poor contact transfer of the ink from anilox roll to printing plate and to substrate. However, flexographic printing is susceptible to film instability and dewetting, which leads to defects including open lines, overlapped lines and edge waviness effects. Controlling the waviness of the printed line is important for applications that have high requirement in pattern geometry, e.g. antennas. These issues can be overcome by adjusting the load pressure and cavities aspect ratio.104-106 Higuchi et al. printed large area of CNTs-based thin film transistors (TFTs) with flexographic printing and the TFTs achieved high mobility of 157 cm2V-1s-1. A thin film electrochemical sensors is developed by flexographic printing of multi-walled CNTs (MWCNTs) on polycarbonate film, showing greater detection ability towards dopamine/dopamine-o-quinone compared with other electrodes.107
1.4.1.3. Micro-contact Printing (μCP)

Micro-contact (μCP) printing needs a conformal contact of patterned elastomeric stamp with the target surface for successful transfer of patterns. It enables patterning of multiple copies of 2D patterns by using patterned stamp developed from master mold. Poly(dimethylsiloxane) (PDMS) is the widely used material in contact printing due to its conformability to large area, ability to have conformal contact with nonplanar surface, elasticity for easy release, low surface energy, chemical inertness, homogeneity, isotropy, optical transparency and durability for multiple usages. The receiving substrate’s surface energy must be higher than that of the stamp to make sure the ink can be successfully transferred. Besides, the stamp needs to be flexible enough and have sufficient mechanical strength to ensure the topographical pattern transferred to the substrate. Béduer et al. achieved ~2 μm wide CNTs line by spray coating CNTs on PDMS mold first and then transferred on SiO2 substrate by micro-contact printing. Hsieh et al. proposed an interesting method to align the NWs/NTs in the process of contact printing. After the NWs/NTs are transferred on the PDMS substrate, the PDMS substrate is stretched to align ~90% of the NWs/NTs within ± 15° to the primary stretching direction. Then the aligned NWs/NTs are contact transferred to the target substrate for applications. With aligned NWs/NTs, the as-developed transistors showed enhancement in transistor mobility, 10-fold reduction in subthreshold slope and superior air stability compared to a pristine polymer host.
Figure 1.10 (a) Schematic of gravure printing process for fabrication of fully printed SWCNTs-based TFTs. 102 (b) Large area of CNTs-based TFTs printed by gravure printing. 96 (c) Schematic of flexographic printing setup. 94 (d) Large array of high mobility CNTs-based TFTs printed by flexographic printing. 108 (e) Schematic of micro-contact printing for fabrication of ~2 µm wide features. (f) High resolution CNTs patterns obtained by micro-contact printing. 112
1.4.2. Noncontact Printing Techniques

The prominent non-contact printing techniques includes screen printing and inkjet printing. Comparing with contact printing, non-contact printings have received greater attractions due to their distinct capability such as simplicity, affordability, speed, adaptability to the fabrication process, reduced material wastage, high resolution of patterns and easy control by adjusting few process parameters.

1.4.2.1. Screen Printing

Screen printing is the most popular and matured technology for printed electronics. Screen printer has simple setup including mesh screen, squeegee, press bed and substrate. And it could also be adapted to R2R with a rotary design.\textsuperscript{93} The ink poured on the screen is squeegeed to move across the screen to transfer it through the stencil openings to the substrate beneath. Although screen printing is a very simple process, the printed pattern quality and characteristics are affected by various factors, such as ink viscosity, mesh size, printing speed, angle and geometry of the squeegee, gap between the screen and substrate.\textsuperscript{113-114} Screen printing is usually compatible with high-viscosity inks because lower viscosity inks are tend to run through the mesh rather than being squeegeed to the substrate.\textsuperscript{115-116} The general resolution of printed pattern by screen printing is 30 – 100 μm with limited wet thickness of a few micron. Reducing the substrate surface energy results in reduced wettability of the ink and it can improve the line resolution. By carefully engineering the surface energy of the substrate to be lower than the surface energy of the ink, good resolution can be achieved even with low viscosity inks.\textsuperscript{116-118} Ink with lower viscosity have higher degree of flowability. It helps reducing the possibility of screen mesh blockage and enable fine edge and smooth surface of the printed line. Recently, 6 μm resolution screen printing has been reported by
improving the quality of the screen mesh. Cao et al. realized scalable screen printing of large area SWCNTs TFTs (fully printed). Cai et al. developed fully printed TFTs with unsorted CNTs as electrode and high purity SWCNTs as semiconductor. The channel length is 150 μm and the as-printed TFTs can be stretched up to 60%. Liang et al. customized a water-based silver nanowire (AgNW) for screen printing. The AgNW ink has viscosity of 124 Pa s at NW concentration of 6.6 wt%. The resolution of printed AgNW pattern is ~50 μm and it showed excellent conductivity of 4.6 x 10⁴ S cm⁻¹, maintaining high conductivity > 10⁴ S cm⁻¹ at 70% tensile strain. A stretchable TFTs array is developed with the screen printable AgNW ink.

1.4.2.2. Inkjet Printing

Inkjet printing is a rapid emerging technique for direct patterning of solution-based ink on various substrates through a micrometer-sized nozzle head. Several actuation mechanisms of the inkjet printing have been extensively developed, including thermal, piezoelectric and electrohydrodynamic (EHD) inkjet systems. Droplets of very small dimensions are ejected at the corresponding pulse generated by either thermal or piezoelectric actuators used in the inkjet nozzle, known as Drop-on-Demand (DoD) mode. In EHD inkjet, ink is ejected by generating a high electric field between the nozzle and substrate. DC voltage results in an intact cone jet while AC voltage results in DoD mode. Inkjet printing enables low cost, low material wastage, low temperature and flexible production of electronic components. The narrowest feature line width obtained with inkjet printing nanoparticle materials without surface treatment is within 14 - 25 μm. By patterning of substrate surface energy, the resolution could be down to ~5 μm. However, due to the high aspect ratio nature of 1D functional material that easy to form clusters and clog the nozzle, inkjet printing of such materials is challenging, resulting in a lower printing
resolution. Multi-walled carbon nanotubes (MWCNTs) were printed by a desktop bubble-jet printer (Canon BJC 4550) with a highest resolution of ~70 μm.\textsuperscript{127} SWCNTs fine line were printed by two parallel nozzles with a line width of ~ 80 μm.\textsuperscript{128} Homenick et al. developed inkjet printing that could be combined with gravure printing and integrated into R2R process, realized large scale printing of SWCNTs-based TFTs.\textsuperscript{129} In their work, silver particle gate electrodes are printed by gravure printing and SWCNTs as semiconductor are printed by inkjet printing. Highly conductive AgNW line were printed by inkjet printing with a sheet resistance of 8 Ω sq\textsuperscript{-1}, but the resolution is only 1 mm.\textsuperscript{130} EHD inkjet printing enables printing high resolution patterns and overcome the nozzle size limitation. With larger nozzle, the chance of nozzle clogging is decreased. Jin et al. used nozzle with 200 μm capillary diameter (outer diameter) to print MWCNTs with a smallest line width of 89 μm.\textsuperscript{131} They also mentioned, by optimizing the concentration and viscosity of the ink as well as the printing speed, MWCNTs line with width of tens of micrometer is possible. In addition to the mentioned inkjet printing methods, researchers are also exploring “Aerosol” of 1D material. CNTs are printed as semiconductor layer for TFTs and LEDs for flexible application.\textsuperscript{132-135}
Figure 1.11 (a) Schematic of screen printing of customized AgNW ink. (b) AgNWs-based TFTs array printed by screen printing wrapping around finger.\textsuperscript{124} (c) Combined R2R printing system of gravure printing and inkjet printing. (d) A single TFT cell that printed by gravure printing (electrode) and inkjet printing (semiconductor).\textsuperscript{130} (e) Close look of aerosol inkjet printing. Inert gas stream carries the functional ink to substrate. (f) SEM image of printed metallic CNT source/drain thin-films after 10 printing passes.\textsuperscript{133}
1.5. Scope and Technical Roadmap

The aim of this dissertation is to use silver nanowires as functional material to develop wearable sensors/electrodes and develop novel techniques to directly pattern AgNWs for wearable electronics integration. This dissertation is consisting of six chapters. In Chapter 1, a comprehensive review on stretchable electronics is presented in the aspect of the nanomaterials, manufacturing mechanisms, printing techniques.

Chapter 2 presents a flexible and stretchable touch cell based on AgNW/PDMS conductors. Such thin polymer-based sensors allow conformal contact with human skins. Two kinds of patterns are introduced and discussed of their performance under bending and stretching. Finite element analysis was also conducted to give a better understanding on the performance of the prepared touch cells. The touch cells showed reasonable performance under bending (bending radius of 10 mm) and strain (up to 20%), enabling its potential application in wearable human-machine interface applications.

Chapter 3 introduces a novel AgNWs patterning technique enabled by EHD printing. In this work, AgNW-based ink was customized to be adapted to the printing technique. Massive parameter studies were conducted to find the best combination of several key factors of the printing result, including AgNW ink viscosity, stand-off distance, back pressure, voltage and printing speed, etc. Surface modification was conducted to ensure the excellent wetting of the ink on various substrates. Th printed AgNW lines was characterized under bending and stretching test, and the excellent performance showed the potential in directly printing of wearable electronics. Additionally, a wearable heater and dry ECG electrode were prepared and their performance was demonstrated on human body.
Chapter 4 includes fundamental study in temperature coefficient of resistance (TCR) of AgNW percolation network with different nanowire densities. Also, thermal annealing effect on TCR of the AgNW films are examined and explained. Kirigami structured was utilized to build a high stretchable wearable temperature sensor. FEA simulation was conducted to provide better understanding on how effective the local strain being released from the deformation of kirigami structure. The performance of the as-prepared wearable temperature sensor was tested and compared with a commercially available temperature sensor.

Chapter 5 gives a summary of the primary findings of this work and suggested potential research following this work.
Chapter 2

Design and Operation of Silver Nanowire Based Flexible and Stretchable Touch Sensors

2.1. Introduction

The demand for touch screen panels has seen dramatic increase in applications such as mobile phones, tablets, and home appliances. It is thus of significant technological importance to develop highly sensitive touch screens. The early touch screen devices mostly rely on resistive sensing, which has several limitations. For instance, it requires physical pressing on the screen, which could cause surface damage/degradation. More recently, devices using capacitive, acoustic, and infrared sensing have been developed. Today, the widely used commercial touch screen panels are based on projected capacitive touch technology owing to their durability, optical clarity, and multitouch capability.

Indium tin oxide (ITO) is the dominant electrode material used in touch screen panels due to its high conductivity and transparency. However, the brittleness, expensive vacuum-deposition process, and dwindling reserve of ITO limit its further application. Nanomaterials have shown promising potential as alternative electrode materials, including carbon nanotubes (CNTs), graphene, metal nanowires, and other metal nanostructures. Wu et al. reported that single-walled CNTs show a comparable transparency and conductivity to ITO. Graphene electrodes were reported to achieve ~30 Ω sq⁻¹ and 98% optical transmittance. Silver nanowires (AgNWs) are emerging candidates. Recently, researchers have fabricated AgNW electrodes with 20 Ω sq⁻¹ and 80% optical transmittance.

Commercial touch screen panels are mainly based on hard (e.g., glass) and flexible substrates (e.g., PET). In recent years, wearable devices have attracted significant attention. In addition to flexibility, stretchability is required to place the wearable devices comfortably on
curvilinear and moving surfaces such as joints, and for them to withstand repeated mechanical deformations such as bending and twisting.\textsuperscript{148-151} Hence, it is of relevance to develop touch sensors on stretchable substrates. Stretchable touch sensors in the pattern of parallel-plate capacitor have been recently demonstrated.\textsuperscript{65, 152-153} However, their capacitances increase considerably with the applied strain.

In this work, we present flexible and stretchable touch sensors with two different patterns (interdigitated and diamond-shaped capacitors to be described later). The touch sensors were made of screen-printed AgNW electrodes embedded in polydimethylsiloxane (PDMS). For each pattern, the simulation-based design was first conducted to choose optimal dimensions for the highest touch sensitivity, followed by the fabrication of the designed sensors. The prototype sensors were characterized when undeformed and deformed (e.g., under bending and stretching) for comparison of sensor performances. The attributes of each pattern are discussed in terms of touch sensitivity and stability under bending and stretching. Note that while AgNW-based touch sensors could be transparent, this paper focuses on the flexibility and stretchability.

2.2. Design and Optimization

Patterning of sensor electrodes is important to maximize the touch sensitivity as the capacitance change upon touch is typically very small, e.g., in the order of fF. The parallel-plate pattern has been used in stretchable touch sensors but its stability under tensile strain is limited.\textsuperscript{65, 152, 154} In addition, it requires two layers of electrodes separated by a dielectric layer. Diamond-shaped pattern is popular due to its high sensitivity,\textsuperscript{140} but it also requires two layers of electrodes and a dielectric layer in between.\textsuperscript{154} On the other hand, the interdigitated pattern possesses reasonable sensitivity and the two electrodes are on the same layer, which makes the whole device
thinner than the other patterns. In this work, we will investigate both the interdigitated and diamond-shaped patterns.

Finite element analysis (FEA) was carried out to design and optimize the sensor dimensions using ANSYS APDL 14.5. FEA is important here as it accounts for the fringing effect in calculating the capacitance. The elements used to define the electrodes and the media are Structural Mass Tet 187 and Electrostatic Tet 123, respectively. The dielectric constants used are 2.6 for PDMS and 1 for air, respectively. Two conductors are defined in the model to represent the two electrodes in a capacitor and the third conductor is defined for a finger (or a conducting object) that touches the capacitor. The third conductor is grounded. In the following, the interdigitated design is presented first, followed with the diamond-shaped design.

2.2.1. Interdigitated Pattern

Figure 2.1 Schematic of the interdigitated and diamond-shaped touch sensors. (a) Parameters simulated in the interdigitated touch sensor including the finger length \( l \) and the finger width \( w \). (b) Parameters simulated in the diamond-shaped touch sensor including the square size \( d \), the middle strip width \( w \) and the effective square length \( s \). For the bending and stretching tests, both sensors are bent and stretched in the horizontal direction. Note that the dashed lines in (a) and (b) represent the footprints of the touch sensors (the same as the PDMS matrices). Both sensors were stretched in horizontal direction.
Figure 2.1 (a) shows a schematic of the interdigitated touch sensor. The interdigitated design includes a 0.1-mm-thick layer of AgNW electrodes that are embedded in PDMS (~0.50 mm in thickness). To optimize the touch sensitivity of the touch sensor, the dimensions of the electrode finger were varied in the simulations while the sensor footprint was maintained as 18 × 18 mm. Here the touch sensitivity is defined as the difference in capacitance between almost touch (i.e., when the finger or conducting object is 1 mm above the sensor) and direct touch (i.e., when

Figure 2.2 Top and side views of the interdigitated and diamond-shaped touch sensors as designed. (a) Simulation setup for the interdigitated sensor model. The sensor includes one layer of AgNWs. (b) Simulation setup for the diamond-shaped sensor model. The sensor includes two layers of AgNWs. Note the diamond-shaped touch cell is thicker than the interdigitated one.
it physically touches the sensor). In the FEA model as shown in Figure 2.2(a), an 8 mm layer of air block is included above the sensor to capture the fringe field between the sensor and the finger. A 10-mm-diametered cylinder represents the finger with a varying height (7 or 8 mm) to calculate the capacitance when the finger is 1 mm above or touches the sensor. The design objective is to achieve the highest possible touch sensitivity.

The first design parameter is the electrode finger length (l) as marked in Figure 2.1(a). In this work, the finger length was varied from 8 to 14 mm (equivalent to overlap from 1 to 13 mm). As shown in Figure 2.3(a), the touch sensitivity rapidly increases up to the point when the electrode finger is 10 mm long. Beyond that, the touch sensitivity shows limited increase. The touch sensitivity increases with the overlap length between the electrode fingers due to the increased fringing field. However, after the overlap exceeds the cylinder (touch finger), the change in the fringe field does not affect the touch sensitivity considerably.

The next design parameter is the electrode finger width (w) that was varied from 0.6 to 2.4 mm. As shown in Figure 2.3(b), the touch sensitivity is peaked when the width reaches 1.5 mm. During this parametric study, to keep the touch cell footprint, the spacing between the fingers reduces with increasing finger width. There is a tradeoff between the finger width and the spacing between the fingers. A wider finger leads to a more extended fringe field, which is disturbed more by the finger touch and thus a higher touch sensitivity. On the other hand, a smaller spacing leads to a larger capacitance before finger touch and thus decreases the touch sensitivity. In the optimized sensor design, the electrode fingers are 1.5 mm wide and 13 mm long as a result of the above parametric study. For the optimized sensor dimensions, the capacitance values were 29.28 and 28.43 fF for almost touch and direct touch, respectively, with the touch sensitivity of 0.85 fF.
Figure 2.3 Parametric study of the interdigitated touch sensor. (a) Sensitivity results based on the electrode finger length varied from 8 to 14 mm. (b) Sensitivity results based on the electrode finger width varied from 0.6 to 2.4 mm.
2.2.2. Diamond-shaped Pattern

Figure 2.1(b) shows a schematic of the diamond-shaped touch sensor. The diamond-shaped design includes two layers of AgNW electrodes (0.1 mm in thickness each). The electrodes are embedded in PDMS and are separated by a layer of PDMS (~0.95 mm in thickness). Similar to what was done for the interdigitated electrode design, several dimensions of the diamond electrode were varied. During the simulations, the electrode footprint (18 × 18 mm) was kept constant. The same 8-mm-thick air block was included to simulate the device boundary and capture the fringe field around it.

The first design parameter is the square length (d) as marked in Figure 2.1(b). This dimension was varied from 3 to 9 mm. As shown in Figure 2.4(a), the increase in the square dimensions leads to higher touch sensitivity. According to Lee et al., the region between two squares of each diamond electrode concentrates the fringing field and is therefore the highly sensitive region for touch.\textsuperscript{155} According to Hwang et al., the sensitivity is proportional to the effective square length (s).\textsuperscript{157}

Next, the width of the middle strip (w) that connects the two squares in the diamond electrode was varied. As it can be seen from Figure 2.4(b), the sensitivity increased initially with the middle strip width and then varied between 3.13 and 3.17 fF. According to Hwang et al., the touch sensitivity is directly proportional to the middle strip width and the effective square length, as mentioned before.\textsuperscript{157} However, the wider the middle strip the smaller the effective square length (s), which can be seen as a tradeoff.

The optimized diamond pattern had a square length of 8 mm and not 9 mm because of the ease in fabrication and a central strip width of 1.4 mm. For the stipulated electrode dimensions,
the capacitances are 26.43 and 23.26 fF for almost touch and direct touch, respectively, with the sensitivity of 3.17 fF.

Figure 2.4 Parametric study of the diamond-shaped touch sensor. (a) Sensitivity results based on the electrode square size varied from 3 to 9 mm. (b) Sensitivity results based on the electrode middle strip varied from 0.4 to 1.5 mm.
2.2.3. Effect of Touch Finger Size

The optimized dimensions of both patterns depend on the size of the touch finger. To generalize the optimization results, the cylinder diameter used in the FEA was varied in a wide range (i.e., from 4 to 16 mm to represent a wide variation of touch finger size, for instance, from children to adults, from fingertip to finger pad, and from little finger to thumb). The electrode parameters for both designs were varied once again and the optimized dimensions were found for each finger size. Figures 2.5(a) and 2.5(b) show the results of the interdigitated design and the diamond design, respectively. In Figure 2.5(a), the electrode finger length is more susceptible to touch finger size whereas the optimized electrode finger width remains nearly constant. In Figure 2.5(b), the optimized middle strip width varies from 1.4 to 1.6 mm while the optimized square length remains constant. The results showed that the diamond design has a more stable performance for a range of human finger sizes when compared to the interdigitated design. In the experimental work to be described below, we will focus on the optimized designs for the 10-mm-diametered touch finger.
Figure 2.5 Optimized dimensions as functions of the touch finger diameter. (a) Optimized finger length and width for the interdigitated pattern as function of touch finger diameter. (b) Optimized square size and middle strip width for the diamond pattern as function of touch finger diameter.
2.3. Fabrication

To fabricate the touch sensors, AgNW conductors with the optimized dimensions for the interdigitated and diamond patterns were screen printed on top of a Si substrate through a prepatterened PDMS shadow mask. Fabrication steps are shown in Figure 2.6 (a) and (b) for interdigitated shape and diamond shape touch cells. More details on the fabrication processes of the AgNW electrodes were reported previously. Liquid PDMS (mixing the “base” and the “curing agent” at a weight ratio of 10:1) was then cast on the Si substrate over the prepared AgNW electrodes, and cured at 100 °C for 35 min in a degassed oven. All the patterned AgNW electrodes were embedded just below the PDMS surface when the composite was peeled off from the Si substrate. Eutectic gallium–indium (EGaIn, Aldrich, ≥99.99%) liquid metal was applied to the ends of each electrode to serve as conformal electric contacts. After that, copper wires were embedded inside the liquid metal and covered by a new layer of PDMS of the same thickness, followed with a curing step. Up to this step, the interdigitated pattern sensor was fabricated. The diamond pattern was fabricated by positioning the AgNW/PDMS film (without the new layer of PDMS on top) orthogonal to another identical AgNW/PDMS film face to face with a thin layer of liquid PDMS in between, followed by a curing step. Both interdigitated and diamond-shaped sensors, as-fabricated and bent, are shown in Figure 2.7.
Figure 2.6 Schematic of fabrication process of (a) interdigitated and (b) diamond-shape touch cells.
2.4. Results and Discussion

The capacitance was measured by an AD7152 capacitance-to-digital converter (CDC) evaluation board (Analog Devices), which has the offset calibration function to compensate parasitic capacitance from the lead wires and the surrounding environment. A cylindrical metal bar with a diameter of 10 mm was used as the touch finger as in the simulation. The bar was grounded to mimic the human touch. The capacitance of the interdigitated sensor cell was measured at 28.32 and 27.42 fF for almost touch and direct touch, respectively. The capacitance of the diamond-shaped sensor cell was measured at 26.35 and 23.14 fF for almost touch and direct touch.
touch, respectively. These results are in good agreement with what we obtained from the simulations.

Furthermore, the interdigitated and diamond-shaped sensors were characterized under bending and stretching. In the bending study, the sensor was wrapped around a cylinder with a radius of 6.5 mm. The capacitance of the interdigitated sensor cell was measured at 30.27 fF for almost touch, decreasing to 29.03 fF for direct touch. Compared with the interdigitated one, the diamond sensor cells showed a larger change in capacitance, dropping to 16.25 fF for almost touch and 14.86 fF for direct touch.

Figure 2.8 (a) AD7152 capacitance-to-digital converter (CDC) evaluation board. (b) Functional block diagram of AD7152.

Furthermore, the interdigitated and diamond-shaped sensors were characterized under bending and stretching. In the bending study, the sensor was wrapped around a cylinder with a radius of 6.5 mm. The capacitance of the interdigitated sensor cell was measured at 30.27 fF for almost touch, decreasing to 29.03 fF for direct touch. Compared with the interdigitated one, the diamond sensor cells showed a larger change in capacitance, dropping to 16.25 fF for almost touch and 14.86 fF for direct touch.
Table 2.1. Capacitance values and touch sensitivity for the interdigitated sensor.

<table>
<thead>
<tr>
<th></th>
<th>Almost Touch (fF)</th>
<th>Direct Touch (fF)</th>
<th>Sensitivity (fF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulation (undeformed)</td>
<td>29.28</td>
<td>28.43</td>
<td>0.85</td>
</tr>
<tr>
<td>Experiment (undeformed)</td>
<td>28.32</td>
<td>27.42</td>
<td>0.90</td>
</tr>
<tr>
<td>Simulation (bending)</td>
<td>30.15</td>
<td>28.96</td>
<td>1.19</td>
</tr>
<tr>
<td>Experiment (bending)</td>
<td>30.27</td>
<td>29.03</td>
<td>1.24</td>
</tr>
</tbody>
</table>

Table 2.2. Capacitance values and touch sensitivity for the diamond-shaped sensor.

<table>
<thead>
<tr>
<th></th>
<th>Almost Touch (fF)</th>
<th>Direct Touch (fF)</th>
<th>Sensitivity (fF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulation (undeformed)</td>
<td>26.43</td>
<td>23.26</td>
<td>3.17</td>
</tr>
<tr>
<td>Experiment (undeformed)</td>
<td>26.35</td>
<td>23.14</td>
<td>3.21</td>
</tr>
<tr>
<td>Simulation (bending)</td>
<td>16.33</td>
<td>14.99</td>
<td>1.34</td>
</tr>
<tr>
<td>Experiment (bending)</td>
<td>16.25</td>
<td>14.86</td>
<td>1.39</td>
</tr>
</tbody>
</table>

Table I lists the simulated and measured capacitance values for the interdigitated sensor when undeformed and bent. Both capacitances and touch sensitivity under bending do not change noticeably when compared to those when undeformed. This result shows that the capacitive sensor can maintain similar performance even when it is bent.
Table II lists the simulated and measured capacitance values for the diamond-shaped sensor when undeformed and bent. The diamond pattern shows a larger variation in capacitances and touch sensitivity when bent compared to the interdigitated design. Since the diamond pattern consists of two electrode layers, it might be more susceptible to capacitance changes due to the relative motion between the layers under bending. This observation is consistent with the simulation results.

Furthermore, both types of sensors were stretched up to 15% strain. The capacitances as functions of the applied strain are shown in Figs. 7(a) and 7(b). For the interdigitated sensor, the capacitance values for both almost touch and direct touch decreased with increasing strain, but the difference between almost touch and direct touch was nearly independent of the strain, suggesting a stable sensitivity over a large range of stretching strain. The average of the capacitance difference was 0.92 fF with a standard deviation of 3.14%, which is in a good agreement with the difference of 0.90 fF when the sensor was not deformed. For the diamond-shaped sensor, the capacitance values remained almost constant up to 15% strain. The average of the capacitance difference was 2.98 fF with a standard deviation of 6.81%, which is in a good agreement with the difference of 3.21 fF when the sensor was not deformed.

Based on the above results, the diamond-shaped pattern showed better touch sensitivity than the interdigitated one when undeformed, bent or stretched. For the interdigitated pattern, the touch causes a 3.18% decrease in capacitance when the sensor is undeformed. When the sensor is curved, it shows a decrease about 4.10% in capacitance. The undeformed diamond pattern shows an excellent performance, with a 12.18% drop in capacitance when directly touched. When the diamond sensor is curved, it still shows an 8.55% decrease in capacitance. When the two patterns are stretched, their touch sensitivities are nearly unchanged when compared to the undeformed
state. On the other hand, the interdigitated pattern showed better stability than the diamond-shaped pattern. The interdigitated pattern maintained nearly the same performances when undeformed, bent or stretched, while the diamond-shaped pattern showed much decreased sensitivity under bending.

The long-term stability of the sensors is of paramount importance for wearable applications. The interdigitated and diamond-shaped sensors were tested under cyclic loading up to 15% tensile strain. The capacitances of both types of sensors remained nearly the same after 2000 cycles. Degradation of AgNW electrodes over time due to oxidation can compromise the device performance.\textsuperscript{159-160} Compared to unprotected AgNW electrodes (i.e., AgNWs on top), Lee et al. found that fully embedded AgNW electrodes in PDMS kept the same resistance for a much longer period of time under UV light.\textsuperscript{160} Besides, our electrodes work as capacitors, which are less prone to the resistance change of the electrodes. Hence, our touch sensors should be robust against oxidation. Indeed, our sensors showed similar performances three months after their fabrication.

The sensors presented in this paper were not transparent. Transparency is critical for wearable touch sensors. Kim et al. showed that more uniformly distributed AgNW networks with lower density are key to transparent electrodes with reasonable conductivity.\textsuperscript{161} In addition, as mentioned above our capacitance-based sensors are not affected much by the resistance change of the electrodes. For future work, we aim at developing transparent and wearable touch sensors with similar performances as presented here.
2.5. Conclusions

Flexible and stretchable touch sensors with two different patterns (interdigitated and diamond-shaped capacitors) were designed, fabricated, and tested. The sensors were made of screen-printed AgNW electrodes embedded in the PDMS matrix. The interdigitated pattern possesses the advantage of just using one layer of AgNWs (instead of two used in the diamond-shaped pattern). The experimental and simulated results showed that the diamond pattern is more sensitive than the interdigitated one in all cases (e.g., undeformed, under bending or under stretching). For both types of sensors, the touch sensitivity remained nearly constant under stretching up to 15% strain, but varied under bending especially for the diamond-shaped ones. They also showed robust performances under cyclic loading and against oxidation. The demonstrated flexible and stretchable touch sensors have potential to be integrated in wearable devices. Future work would include development of larger-area, transparent, and wearable touch sensors.
Chapter 3

Electrohydrodynamic Printing of Silver Nanowires for Flexible and Stretchable Electronics

3.1. Introduction

Flexible and stretchable conductors, a key component in flexible and stretchable electronics, have garnered significant attention from the scientific community and industry. Metal nanowires (NWs) in the form of random percolation network have shown excellent potential as flexible and stretchable conductors.\textsuperscript{6, 50, 53, 58, 70, 162-168} For a random network at a given material density, longer NWs can lead to higher electric conductivity according to the percolation theory and larger stretchability, which are desirable for flexible and stretchable conductors. Longer NWs can also help achieve a better balance between electric conductivity and optical transmittance (\textit{i.e.} increasing electric conductivity without reducing optical transmittance), critical for transparent electrodes made of metal NWs.\textsuperscript{50}

Printing is a powerful technique to enable the production of large-scale, low-cost electronic devices and systems. Most of the existing methods for fabricating metal NW conductors are based on solution coating and deposition, including drop casting, spinning coating, spray coating, and Meyer rod coating.\textsuperscript{6, 54, 169-170} Recently contact printing methods such as gravure printing and screen printing have been reported for printing silver NWs (AgNWs).\textsuperscript{103, 123, 171} While these methods can achieve high-speed and large-scale printing, the resolution and/or the electric conductivity of the product is typically limited. Moreover, non-contact printing technologies that do not use a cliché have the advantage over contact printing of allowing on-demand patterning.

Inkjet printing, a representative form of non-contact printing, is widely used for printing electronic devices.\textsuperscript{130, 172-173} Inkjet printing of long metal NWs (typically >10 μm), however, is challenging due to the risk of nozzle clogging and the difficulty to maintain the structural integrity.
of the NWs through the printing process. The resolution of ink-jet printing technology is mainly limited by the size of the printer nozzle, with the printed droplets at the same scale of nozzle size. For ink-jet printing as a general “rule of thumb,” the size of the particles in the ink is suggested not to exceed 1/100 times the diameter of the printhead nozzle, so as to reduce the risk of nozzle clogging. Considering the length of typical AgNWs to be >10 \( \mu \text{m} \), it is extremely difficult for inkjet printing to produce high-resolution features. Recently there have been a few studies of applying inkjet printing for metal NWs, however, the resolution in these studies is generally at sub-mm scale, which is far from the requirement of advanced electronic devices. Electrohydrodynamic (EHD) printing is an emerging technique that offers a high-resolution printing, which can produce jet or droplet that is much (up to a few orders of magnitude) smaller than the nozzle diameter. Due to this unique capability, large nozzle can be used in EHD printing to produce micro-scale features and also evade the dilemma of printing resolution and nozzle clogging.\textsuperscript{124, 174-176} Moreover, as a direct printing approach, EHD printing does not require a mask for device fabrication. EHD printing was recently used to print AgNWs. But that work focused on aligning AgNWs at very low NW density and the printed pattern was not conductive.\textsuperscript{177}

Herein, A high-resolution, large-scale printing of highly conductive AgNWs for flexible and stretchable electronics using EHD printing is presented. AgNW ink was designed and synthesized for EHD printing. The smallest line width obtained in this work was \(~45 \mu \text{m}\). After post treatment, printed AgNWs showed an electric conductivity as high as \(~5.6\times10^6 \text{ S/m}\). Flexibility and stretchability of the printed patterns were characterized under cyclic bending and stretching tests. Devices based on the printed AgNWs were demonstrated including flexible heaters and stretchable dry electrodes for electrophysiology.
3.2. Experimental Section

3.2.1. EHD Printing Setup

The EHD printing system included three sub-systems: a pneumatic dispensing system, a voltage supply system, and a precision three-axis translation stage. Figure 3.1 shows the schematic of the printing system. The pneumatic system that includes air pump, precision regulator was used to provide pressure to the AgNW solution to facilitate the ink flow from the printing nozzle. The voltage supply (Trek Model 610E, Trek, Inc.), providing a maximum voltage of 10 kV, was connected to the printing nozzle and the ground electrode on which the substrate sits. The precision three-axis stage was installed on an anti-vibration table to reduce vibrational noises. Three linear actuators were connected to the precision stage in XYZ directions, offering an accuracy of 100 nm in each direction. A side-view camera with a best resolution of 0.5 μm was used to monitor and

![Figure 3.1 Schematic of EHD printing setup.](image-url)
record the printing process. Figure 3.3a shows repeated patterns printed by EHD printing in a large scale, indicating the potential of this technique for large-scale, high-resolution printing of AgNW devices. Figure 3.3b shows two examples of complicated patterns. More examples of patterns printed by EHD printing were shown in Figure 3.18b, Supporting Information.

Figure 3.2 Photograph of EHD printing setup.
3.2.2. AgNW Ink Customization

AgNW ink was synthesized and customized for EHD printing. Important ink parameters include viscosity and AgNW concentration. DI water was used as the major solvent. Poly (ethylene oxide) (PEO) was added to the ink to tune the viscosity. The rheological behavior of AgNW inks with different PEO concentrations (3%, 4%, 5% weight ratio) was investigated. All three inks displayed a shear thinning thixotropic behavior. AgNW ink with higher PEO concentration exhibited higher viscosity at the same shear rate. For instance, the viscosities at shear rate of 1 s\(^{-1}\) for PEO concentration of 3 %, 4 % and 5 % were 1.89, 4.28 and 8.61 Pa·s, respectively (Figure 3.4a). In this work, 4 wt.% PEO was selected; higher PEO concentration could cause nozzle clogging, while lower concentration could reduce the printing resolution. Higher AgNW concentration can improve the conductivity of the printed pattern, but might cause AgNW clustering in the ink, increasing the possibility of nozzle clogging. On the other hand, higher AgNW concentration might decrease the printing resolution as more NWs can be dragged out of

Figure 3.3 (a) Large-scale of AgNW patterns printed by EHD printing. Scale bar, 1 cm. (b) Two complicated AgNW patterns with high resolution. Scale bar, 5 mm.
the nozzle during printing (Figure 3.4b). In this work, AgNW concentration of 15 mg/ml was selected.

![Figure 3.4](image)

**Figure 3.4** (a) Shear viscosity of the three different AgNW ink formulations. (b) Printed line width vs. AgNW concentration in the ink.

The AgNW ink was obtained from mixing the AgNW solution (AgNW concentration is 150 mg/ml in DI water) and PEO solution. The AgNW used has an average diameter of ~120 nm and average length of ~25 μm. The PEO powder (M<sub>v</sub>: 100,000) was purchased from Sigma-Aldrich. PEO powder was first diluted with DI water to form a PEO solution and then mixed it with AgNW solution and stirred for 10 min to achieve the AgNW inks with a AgNW concentration of 15mg/ml and a PEO weight ratio of 4%.
3.2.3. Surface Modification of Receiving Substrates

This EHD printing technique enables direct AgNW patterning on a variety of substrates with high resolution, as long as the substrate surfaces are hydrophilic for stable ink settlement. In this work, AgNW patterns were successfully printed on PDMS (dopamine treated), PET, glass, letter paper, nanofiber paper, polycarbonate filter (Whatman 111103) and nature rubber latex (lab use gloves).

The receiving substrate need to be hydrophilic to be printed by the customized water-based AgNW ink. PDMS is widely used as substrate for wearable device owing to its excellent stretchability, high transparency and good bio-compatibility. However, the low surface tension of PDMS (21-23 mJ m$^{-2}$) is limiting direct printing of AgNW on it. Reduction of the hydrophobicity is required and can be achieved by exposing PDMS to different types of oxidizing plasmas, corona discharges, or UV radiation. Oxygen plasma treatment is the most widely used method to modify the surfaces of PDMS. Such treatment can propagate deep (about several hundreds of nanometer) under the surface of PDMS and cause permanent chemical change in the near surface region of PDMS. Analysis from X-ray photoelectron spectroscopy on plasma-treated PDMS revealed a rapid substitution of carbon atoms by oxygen atoms, which led to the formation of hydrophilic surfaces. Simultaneously, a thin and brittle silica layer is generated on the surface of PDMS and causes mechanical property changed in the treated PDMS. However, Owen et al., also reported the cracks in the thin layer allowed for the migration of low-molecular-weight un-crosslinked PDMS fragments to the surface and cause hydrophobic recovery. UV/UVO treatment causes a similar chemical change to the surface of PDMS but at a much lower speed. The affect PDMS layer has thickness around 10-30 nm. Hence, the stability of such treatment
is not good enough and has the potential to introduce cracks to the surface of PDMS, deteriorating the stretchability of the polymer.

Polydopamine is a bio-inspired material that could change the surface property from hydrophobic to hydrophilic. And it’s a simple process by only soaking the substrate in a dilute aqueous solution of dopamine (1 mg/ml of dopamine in Tris buffer), buffered to a pH value of 8.5. It was found a 5-minute polydopamine treatment is enough to ensure the wetting of customized AgNWs ink on PDMS substrate. The treatment effect (advancing and receding contact angles) of PDMS surface as a function of treatment time are plotted in Figure 3.5. Compared with oxygen plasma and UV/UVO treatment, polydopamine treatment can effectively treat the substrate with long-term stability.

![Figure 3.5](image)

**Figure 3.5** Advancing and receding contact angles of polydopamine treated PDMS surface with different treatment time.
3.2.4. Post Treatment of Printed AgNWs Patterns

Post treatment was performed to improve the conductivity of printed samples. Here, printed AgNW patterns were soaked in DI water for 5 mins to remove PEO and then dried at 50 °C. This process may need to be repeated to remove PEO completely. After post treatment, the smallest line width achieved in this work was ~45 μm. Figure 3.6 shows the resistance change with different treatment times for printed patterned on glass and PDMS substrate.

![Figure 3.6](image)

**Figure 3.6** Resistance change as function of the number of post-treatments for the printed AgNW samples on PDMS and glass substrates.

3.2.5. Packaging of Printed AgNWs Patterns

Packaging is an important process to enable integration of other electronics and protect the printed conductive AgNW patterns. In this work, silver paste, liquid metal (Gallium-Indium eutectic, Sigma Aldrich) and copper wires are used to connect the lead out. For flexible devices, silver paste is used to connect copper wire and printed AgNW pad as bending usually introduce
small strain (<1%) to the film and the bonding between silver paste and substrate (e.g. PET or PI) is strong enough to build promising contacts. However, larger strain (>5%) that stretchable electronics usually experienced cannot withstand by the silver paste/substrate bonding. Liquid metal is used for bonding of copper wire with the printed conductive AgNW pad. However, the liquid does not adhere to the AgNW but can form a strong bonding with polymer substrate (e.g. PDMS). Hence, a surface modification of the printed AgNW pattern is required to enhance the bonding between AgNW and liquid metal, simply by plasma treatment. A plasma cleaner is used (DPC-32G, HARRICK PLASMA) to treat the surface of AgNW. Power of the plasma was set to middle and the treatment time is 60 s. Additional layer of PDMS is required to seal the liquid metal in the designate area.
3.2.6. Flexibility and Stretchability Characterization

AgNW patterns were printed on PET and PDMS for bending and stretching test, respectively. Cyclic bending and stretching test were conducted on a custom-made testing stage (Figure 3.7a). Four-wire measurement was used to measure the sample resistance under cyclic loading using a digital multimeter (34001A, Keysight Technologies) (Figure 3.7b).

![Image](image1.png)

**Figure 3.7** Photograph of (a) customized tensile stage and (b) Multimeter 34001A.

3.2.7. Measurement of Heater and the Test of ECG Electrode

For the measurement of the heater, a DC power was applied to the heater at the two external pads. IR thermometer (A655sc, FLIR) was used to measure the temperature distribution of the heater. For the ECG test, the as-fabricated electrodes were tested on PowerLab 4/25T (ADInstruments, Inc.) simultaneously with commercially available 3M wet ECG electrodes for
comparison. One 3M electrode was used ground/reference electrode, two pairs of AgNW electrode and 3M electrode were attached to left and right chest, serving as positive and negative electrodes.

Figure 3.8 Schematic of ECG measurement setup.

3.3. Results and Discussion

3.3.1. Printing Parameters

The EHD printing process was affected by several parameters, including applied pressure, voltage, stand-off distance (distance between printing head and substrate), printing speed, and nozzle size. Due to the viscosity of the ink and relatively small nozzle used, a small air pressure of 0.4 psi was applied to the system to facilitate the ink flow to the nozzle tip. Applied voltage and the resulting electrostatic field played a crucial role in achieving the high printing resolution. Without the voltage, the ink just flowed out, and accumulated around the nozzle tip to form a ball shape, which produced large droplets leading to low-resolution printing. In this work, to initiate and maintain EHD printing, a voltage of 1500 V was applied between the nozzle and the ground
electrode. The electrostatic force deformed the meniscus into a Taylor Cone, and ejected a fine jet from the Taylor Cone (Figure 3.9), leading to high-resolution printing. Dashed line indicates the external profile of the nozzle. Moreover, both printing speed and stand-off distance affected the printing resolution and stability of the printing process. Higher printing speed and larger stand-off distance provided better printing resolution. As shown in Figure 3.10a, the line width decreased
with the increasing stand-off distance, due to the reduced jet diameter from the Taylor Cone. In the rest of this work, stand-off distance of 75 μm was selected. By increasing the printing speed, the line width decreased (Figure 3.10b); at higher printing speed with the same ink flow rate, a smaller amount of ink per unit length leads to a smaller line width. Printed AgNW patterns had clean and smooth edge as shown in Figure 18a, Supporting Information, which was essential for circuit design, such as transistors and interdigitated sensors.

3.3.2. Morphology of Printed AgNW Patterns

Next, we studied the morphology of the printed NW lines and density of the NWs. SEM images of the NWs at the center and the edge of the printed lines at two different printing speeds (high speed 10 mm/s and low speed 1 mm/s) were shown in Figure 3.11. NW alignment and density can be evaluated from these images. In each case the number of NWs under the same area was counted and the NW orientation was denoted from -90 to 90° with 0° pointing to the printing direction. It was observed that at the higher printing speed, most NWs (70%) are oriented from -10 to 10° with respect to the printing direction, slightly more aligned along the edges than at the center, due to the liquid drag force from high-speed printing. At the lower printing speed, NWs are distributed more randomly in the center, but more aligned in -10 to 10° along the edge. It is well known that the NWs are randomly oriented forming a percolation network when drop casted.6, 70

The alignment phenomenon observed above can be attributed to the shear flow. The shear flow along the liquid edge helps achieve better NW alignment along the edge than at the center; higher printing speed can result in better NW alignment due to higher shear flow rate. Table 3.1 shows the NW density at the center and along the edge. Here the NW density was calculated by count the number of NWs in a fixed 50 x 50 μm square area.
Figure 3.11 AgNW alignment at center and edge of the printed line when printed at (a) high speed and (b) low speed. Scale bar, 10 μm.
Table 3.1 AgNW density at the center and along the edge at two different printing speeds.

<table>
<thead>
<tr>
<th></th>
<th>Center [μm²]</th>
<th>Edge [μm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-speed (10 mm/s)</td>
<td>0.59</td>
<td>0.58</td>
</tr>
<tr>
<td>Low-speed (1 mm/s)</td>
<td>1.86</td>
<td>1.30</td>
</tr>
</tbody>
</table>

3.3.3. Electrical Properties of Printed AgNW Patterns

Electrical conductivity of the printed AgNW lines was characterized after the post treatment. The patterns used for measurement had the same length of 10 mm but varying line width from 45 to 115 μm, controlled by the printing speed. Four-wire (4W) measurement was used to measure the resistance of each sample accurately. AgNW lines with larger line widths possessed smaller resistances, as shown in Figure 3.12a. Resistance, sheet resistance and conductivity of the samples were measured and calculated by the following method. Resistance was measured by 4-wire measurement. Film thickness and cross-sectional area were measured by a Veeco Dektak 150 Profilometer (Figure 3.21, Supporting Information). Sheet resistance Rs was calculated by Rs=RW/L and electrical conductivity σ was calculated by σ=L/(RA), where R, W, L and A are the measured resistance, line width, line length and cross-sectional area, respectively. Figure 3.12b, c show that as the line width increases, the pattern becomes more conductive. This is mainly because higher printing speed leads to lower density of NWs and hence lower electric conductivity. NW alignment did not appear to play an important role in the electric conductivity in this case. As mentioned earlier, when printing these lines, the only varying parameter was the printing speed, while all other parameters remained constant such as the AgNW concentration and stand-off distance.
Flexibility and stretchability of the printed AgNW conductors were evaluated, which are of importance relevance for their potential applications in wearable electronics. Bending and tensile tests of the printed AgNWs conductors were carried out. AgNWs were printed on a flexible substrate, PET, for the bending tests. The bending angle started from 0 ° to 180 ° as shown in the inset of Figure 3.13a. Given the thickness of the PET film of 0.12 mm, the maximum strain in the

Figure 3.12 Electrical properties of printed AgNW lines with different line width including (a) resistance, (b) sheet resistance, and (c) conductivity.

### 3.3.4. Mechanical Characterization Under Bending

Flexibility and stretchability of the printed AgNW conductors were evaluated, which are of importance relevance for their potential applications in wearable electronics. Bending and tensile tests of the printed AgNWs conductors were carried out. AgNWs were printed on a flexible substrate, PET, for the bending tests. The bending angle started from 0 ° to 180 ° as shown in the inset of Figure 3.13a. Given the thickness of the PET film of 0.12 mm, the maximum strain in the
AgNWs at bending angle of 180° was estimated to be 0.76% (smallest bending radius is ~2.7 mm). The sample showed a stable resistance reading with 200 cycles of repeated bending to the smallest bending radius of ~2.7 mm (Figure 3.13b). Consecutive images showing the bending process can be found in Figure 3.19.

**Figure 3.13** Stable resistance of printed AgNW patterns under bending and stretching tests. (a) Resistance as a function of bending curvature. (b) Resistance under 200 bending cycles with a bending curvature of 0.37 mm⁻¹ or a radius of 2.7 mm. (c) Resistance as a function of strain under selected stretching and releasing cycles. (d) Resistance under 300 stretching cycles with a maximum strain of 30%.
3.3.5. Mechanical Characterization Under Stretching

For the tensile tests (Figure 3.13c), AgNWs were printed on a PDMS substrate that was pre-strained at 50%, which was then released after post treatment of the printed AgNWs. This pre-straining/releasing step was to generate a wavy AgNW/PDMS structure, which is a commonly used strategy to generate stretchable conductors with nearly constant resistance during subsequent stretching. The as-prepared sample was then cyclic stretched to 30% strain and resistance value was recorded simultaneously. At the beginning of the tests of the wavy AgNW conductor, the resistance increased a little with the increasing number of cycles (i.e. 10.6% increase in 50 cycles) (Figure 3.13d). Afterwards, the resistance showed excellent stability. *In-situ* SEM and optical images were taken during the tensile tests to capture the detailed AgNW/PDMS wavy structure and correlate with the resistance values (Figure 3.20, Supporting Information). From the bending and tensile testing, the printed AgNW-based conductors exhibited excellent flexibility and stretchability, critical for many wearable device applications.\(^{185-188}\)

3.3.6. Wearable Heater for Thermal Therapy

Wearable heater is a promising candidate for thermal therapy.\(^ {189-190}\) In this work, AgNWs printed fractal pattern of Peano curves were demonstrated as a flexible heater. In the fractal pattern, arc sections replace the sharp corners from the mathematically defined fractal layout to improve the elastic mechanics (e.g. flexibility and stretchability). In addition, the fractal pattern of Peano curves can have large area coverage.\(^87\) The footprint of the heater was 6 × 6 mm, as shown in Figure 3.14. Figure 3.14a also shows several consecutively captured infrared (IR) images during an ON-OFF cycle. During the ON stage, a uniform temperature distribution was observed around the AgNWs pattern. Figure 3.14b shows the time-dependent temperature profile of the heater at
Figure 3.14 Printed AgNW heaters. (a) IR images of AgNW heater (scale bar, 5 mm). (b) Temperature vs. time for the AgNW heater showed in (a). (c) IR images of a AgNW heater directly printed on lab-use gloves.
different voltages. The maximum temperature obtained was ~160 °C at the voltage of 25 V, with the maximum heating rate and cooling rate of 21 and 29 °C S⁻¹, respectively. The same heater pattern was also directly printed on lab-use gloves to demonstrate the potential for wearable applications. The heaters exhibited stable heating performance when bent, stretched, and/or twisted. Figure 3.14c shows the IR images of the heater under different deformation modes.

Figure 3.15 IR camera used for thermal analysis of the heater. (A655sc, FLIR)

3.3.7. Dry ECG Electrode for Health Monitoring

Dry ECG electrodes without the electrolytic gel layers as in the conventionally used wet electrodes have received significant interests for long-term health monitoring.¹⁹¹⁻¹⁹² AgNW-based dry ECG electrodes have shown outstanding performances.¹⁹³ Here AgNWs were printed into a
fractal pattern of Greece Cross, which also can effectively release the local strain under stretching, on PDMS substrates as the dry ECG electrodes (Figure 3.16a).\textsuperscript{87} The PDMS substrate has a thickness of 300 μm, enabling conformal contact between skin and conductive layer. As shown in Figure 3.16b, the ECG signal captured from the printed AgNW dry electrode showed excellent performance compared to that obtained from the 3M wet electrode. Since the printed AgNW electrodes are “dry” (i.e. without the electrolytic gel that can cause skin irritation under long-term wear), they are suitable for long-term ECG monitoring.

Figure 3.16 Printed AgNW dry ECG electrode (a) Printed AgNW dry ECG electrodes mounted on chest. The inset shows a magnified image of an electrode. Scale bar, 5 mm. (b) ECG signals collected from AgNW dry ECG electrode and a 3M wet electrode for the purpose of comparison.
3.4. Conclusions

In summary, we report scalable, high-resolution and mask-less printing of AgNWs using EHD printing. The EHD technique enables direct printing AgNWs on a diverse range of substrates, including PDMS, PET, glass, letter paper, nano-fiber paper, and polycarbonate filter. The printed AgNW patterns were highly conductive (with conductivity as high as $\sim 5.6 \times 10^6$ S/m). The printed line width was found to depend on several ink and printing parameters, e.g., ink viscosity, AgNW concentration, stand-off, printing speed, voltage, nozzle size, and pressure. The ink properties and printing conditions were characterized to achieve the optimal printing performance. Post treatment was developed to remove PEO residue and enhance the conductivity. A flexible heater was fabricated showing a uniform temperature distribution with a maximum heating rate of $\sim 21 \, ^\circ\text{C} \, \text{S}^{-1}$ and cooling rate of $\sim 29 \, ^\circ\text{C} \, \text{S}^{-1}$. The AgNW heater was also printed on lab-use gloves and showed stable heating performance under bending, stretching, and twisting. Printed AgNW dry ECG electrodes were able to collect accurate ECG signals, ideal for long-term wearable applications. Fractal-inspired patterns, such as Peano curve and Greek cross, were used to improve the elastic mechanics of the AgNW devices.
3.5. Supporting Information

3.5.1. AgNWs Printed on Various Substrates

Figure 3.17 Optical images of AgNWs lines printed on various substrates. (a) letter paper, (b) glass, (c) nanofiber paper, (d) PDMS, (e) PET, and (f) polycarbonate filter.
3.5.2. Optical Images of Printed Samples

Figure 3.18 (a) Optical image showing the sharp edge of printed AgNWs and dense AgNWs network. Scale bar, 50μm. (b) Additional AgNWs patterns printed on glass slide.
3.5.3. Consecutive Images from Bending Test

Figure 3.19 Consecutive images of bending test from original state to final state. Bending curvatures are marked below the images respectively. Unit, mm\(^{-1}\).
3.5.4. Optical and SEM Images of Wavy Structures

Figure 3.20 Optical and SEM (inset) images of AgNW/PDMS sample under pre-strained and released conditions. Scale bar, 10 μm.
3.5.5. Width and Thickness of Printed AgNWs Lines

Figure 3.21 (a) The thickness of printed AgNWs line decreased as the printing speed increases. (b) Profile images of printed AgNWs line with a width of ~80 μm.
Chapter 4

Stretchable Temperature Sensor Based on Silver Nanowire Composite: Temperature Coefficient of Resistance Measurement and Kirigami Design

4.1. Introduction

Highly sensitive flexible and stretchable sensors that can be used to monitor vital biosignal, such as body temperature, respiration rate, blood pressure, glucose level and electrophysiology signals, have garnered tremendous interest. Such devices can be conformally attached to human skin or integrated with textiles to realize its functionality. Body temperature is one of the most important biosignal, which is closely associated with a variety of illnesses/diseases, e.g., acute stroke, sleep quality, osteoarthritis pain and breast cancer. Additionally, high body temperature speeds up the fatigue in trainers during prolonged exercises. In order to realize long-term monitoring of body temperature, the temperature sensor should be flexible and stretchable in order to be conformally attached to human skin. In particular, the sensor needs to be stretchable to accommodate large strain up to 100% when attached to areas such as knees and elbows.

Thermoresistive effect is typically used for temperature sensing. The resistance of a conductive material changes with temperature due to thermally introduced charge carrier scattering (resistance increase) or thermally enhanced charge transport (resistance decrease). Several stretchable temperature sensors based on the thermoresistive effect have been developed using thin film metals, graphene, and carbon nanotubes (CNTs) and metallic nanowires. However, most of the stretchable sensors suffer crosstalk between temperature and strain as resistance change can be caused by either temperature change or applied strain.
Bulk Ag has a high temperature coefficient of resistance (TCR) of $3.8 \times 10^{-3}/\degree C$ at 20 $\degree C$, which is close to the widely used material for temperature sensor, Pt ($3.9 \times 10^{-3}/\degree C$). Ag nanowire (AgNW) is a promising conductive material that has been widely used in flexible and stretchable devices. Wang et al. found that AgNW and bulk Ag shares the similar phonon-electron scattering and a single AgNW exhibits higher TCR than that of bulk Ag.\textsuperscript{217} Hence, AgNW can be potentially an excellent candidate for flexible and stretchable temperature sensor.

Here, we report a stretchable but strain-insensitive temperature sensor based on a composite material consisting of AgNW network and polyimide (PI) matrix. TCR of the composite film was characterized in the temperature range from 25 to 60 $\degree C$. TCR was found to depend on AgNW density and annealing temperature, that is, TCR increases with increasing AgNW density and increasing annealing temperature. However, it is known that resistance of the AgNW composite depends on the applied strain too. To achieve large stretchability for wearable applications and at the same time true temperature sensing that is insensitive to strain, a Kirigami-inspired structure was adopted. As a result, the sensor can be used under large strain (up to 100%) with no crosstalk from the applied strain. The temperature sensor was used to monitor the skin temperature at bicep and knee under motion, demonstrating outstanding performances of the sensor for wearable applications.
4.2. Experimental Section

4.2.1. AgNWs Ink Preparation

AgNW was synthesized by polyol method. After synthesis, the AgNWs need to be washed by acetone to remove the PVP layer on the surface of nanowires. Additionally, the AgNWs solution need to be centrifuged to remove impurity introduced from synthesis (e.g., nanoparticles, nanorods). The as-synthesized AgNW has an average diameter of 120 nm and an average length of ~25 μm. AgNW was diluted in ethanol with a concentration of 1 mg/ml for the following spray coating.

4.2.2. AgNWs Deposition

An airbrush (A4709, Aztek) was used to deposit the NWs on pre-cleaned glass slides (0215 glass, Corning). The as-prepared AgNW ink was spray-coated with a back pressure of 10 psi (Iwata studio series air compressor) and nozzle-substrate distance of ~15 cm. A hot plate was used during the coating process to speed up the evaporation of AgNW solvent. To achieve uniform coating, the nozzle of the air brush needs to move regularly over the receiving substrate. A multimeter was used to monitor the resistance of the coated glass slide. The resistance value can provide an estimation of the AgNW density coated. After the AgNW density reaches designed value, heat treatment is introduced to enhance the bonding between NWs for sensor fabrication.

4.2.3. Polyimide Coating

Colorless polyimide resin (CP1 polyimide resin, NeXolve) was spin-coated on the prepared AgNW network at 500 rpm for 30 sec. Then the resin was cured at 60 °C for 3 hrs. The thickness
of the prepared AgNW/PI film was ~9 μm measured by Ellipsometer (P-7 profilometer, KLA-Tencor).

4.2.4. Laser Cutting and Packaging

Prepared AgNW/PI film was cut into the designed Kirigami pattern by a laser cutter (VLS6.60, Universal Laser Systems). The cutting parameter are 0.8% power and 50% speed and 1000 PPI in Raster mode. With this setting, the width of the laser-cut trace in AgNW/PI film is ~270 μm. After laser cutting, the AgNW/PI film was released from the glass slide by soaking in DI water. And then the sample was transferred onto a glass slide with the AgNW side faces up. Ag paste and copper wires were used as lead out.

4.2.5. TCR Characterization

AgNW/PI temperature sensors were characterized on a hot plate. A thermocouple thermometer (HH802U, Omega) was used to obtain the local temperature on the AgNW/PI temperature sensor and a digital multimeter (34401A, Agilent) was used to monitor the resistance of the sample by 4W measurement.

4.2.6. Stretchability Characterization

The AgNW/PI temperature sensor was attached on stretchable fabric with TPU film by heat press. TPU is a thermal plastic material with a melting temperature around 150°C. After heat press process, the sample was firmly adhered to the stretchable fabrics and then mounted on a custom-made testing stage for tensile testing.
4.3. Results and Discussion

Fabrication process of the stretchable temperature sensor is shown in Figure 4.1. (a) AgNWs are spray-coated on glass slide. (b) AgNW network on glass slide is thermally annealed. (c) Colorless polyimide resin is spin-coated on the AgNW network and then cured. (d) Cured AgNW/PI film is patterned with Kirigami structure by laser cutting. (e) Ag paste and copper wire are used as lead wire. (f) SEM image of AgNW exposed side. Scale bar is 5 μm.

Fabrication process of the stretchable temperature sensor is shown in Figure 4.1. (i) AgNW ink was spray-coated on a pre-cleaned glass slide to form a AgNW percolation network; (ii) Then the AgNW network was thermally annealed to reduce the contact resistance between AgNWs; (iii) A thin layer of PI resin was spin-coated on the AgNW film, followed by curing; (iv) The cured AgNW/PI thin film was patterned into the designed Kirigami pattern by laser cutting; (v) Finally, the patterned AgNW/PI was peeled from the glass substrate by a water-assisted method. Copper wires were attached at the two ends of the AgNW/PI film as lead wires using Ag paste. The AgNWs were inlaid into the surface layer of the PI film as shown in the SEM image (Figure 4.1f), forming a conductive surface. Compared to AgNWs on top of a film, this inlaid-type of structure is mechanically more robust and more wear resistant.
Figure 4.2 (a) Sheet resistance was measured vs. different AgNW densities after the sample is as-prepared, after 150 °C annealing and 200 °C annealing. (b) SEM images. Comparison of nanowire contact before and after different thermal annealing process. Scale bar: 200 nm. (c) Thermoelectric behavior of the AgNW network with nanowire density of 2.05 nw/μm². The sample was thermally annealed at 200 °C for 30 min. (d) TCR of AgNW networks with different nanowire densities are plotted with TCR of Ag bulk. TCR of the samples after different thermal annealing process are also plotted.
4.3.1. TCR of AgNWs Films

AgNW density and annealing temperature have important effects on TCR of the AgNW films. To identify the optimal AgNW density and annealing temperature, AgNW networks on the glass slides were prepared. AgNWs were spray coated on the glass slide, following step (i) in Figure 4.1a, with different NW densities. The NW density was calculated from optical images, ranging from 0.26 to 2.05 nanowires per μm². The same AgNW networks were thermally annealed in a CVD furnace (TF55035A-1) at 150 °C for 30 min and then at 200 °C for 30 min. Sheet resistance was measured following each annealing step. Figure 4.2a shows that thermal annealing decreased the sheet resistance of the AgNW network. This is because thermal annealing improves the contact between NWs by welding the NW junctions. Hence, the contact resistance in the nanowire network decreases and the AgNW network becomes more conductive. But the resistance change also depends on the NW density. For instance, for the lowest NW density (0.26 per μm²), the sheet resistance decreased from 23.73 Ω sq⁻¹ to 11.38 Ω sq⁻¹ and 3.73 Ω sq⁻¹ after annealing at 150 °C and 200 °C, respectively; while for the highest NW density (2.05 per μm²), it did from 0.73 Ω sq⁻¹ to 0.64 Ω sq⁻¹ and 0.55 Ω sq⁻¹, respectively. SEM images of the AgNW network after thermal annealing are shown in Figure 4.2b, showing the NW junctions formed by thermal annealing. TCR of the AgNW network was extracted from the resistance vs. temperature data. Thermoresistive behavior of the AgNW network (at density of 2.053 per μm²) after 200 °C annealing is shown in Figure 4.2c as an example. The resistance change showed excellent linearity in the temperature range tested (25 – 60 °C). TCR of the AgNW network, which is defined as follows, can be extracted from the thermoresistive curve,

\[ TCR = \frac{1}{R(T_0)} \frac{R(T) - R(T_0)}{T - T_0} \]  

(1)
where $R(T_0)$ is the resistance at $T_0$ (usually room temperature, here taken as 25 °C) and $R(T)$ is the resistance at $T$. TCRs of the five AgNW networks at different densities were calculated with and without the annealing, as plotted in Figure 4.2d together with the TCR of bulk Ag ($3.8 \times 10^{-3}/°C$).

It was found that AgNW network with higher NW density has a higher TCR. Before thermal annealing, the AgNW networks with densities of 0.263 and 2.053 per $\mu$m$^2$ showed TCRs of $2.62 \times 10^{-3}/°C$ and $2.94 \times 10^{-3}/°C$, respectively. It was also found that thermal annealing can increase the TCR of the AgNW network. For instance, for the AgNW network with density of 2.053 per $\mu$m$^2$, TCR increased from $2.94 \times 10^{-3}/°C$ as prepared to $3.24 \times 10^{-3}/°C$ and $3.32 \times 10^{-3}/°C$ after thermal annealing at 150 °C and 200 °C, respectively. These observations can be understood by comparing AgNW network and Ag thin film. AgNW networks with higher density behaves more similar to a thin Ag film. After annealing, the contacts between AgNWs are annealed and the polymer coatings around the NWs (e.g. polyvinylpyrrolidone formed during the AgNW synthesis) are partly removed, so the AgNWs are transformed from a discrete structure (i.e. percolation network) to a more continuous structure, more similar to a thin Ag film. Due to the voids (open space) in the NW network and residue polymer coatings, TCRs of the AgNW networks are lower than that of bulk Ag.

In addition to the sheet resistance and TCR measurements, optical transmittances of the AgNW networks were measured, as shown in Supporting Information. All these measurement results can provide valuable information for selecting the optimal materials for the desired temperature sensors. In this work, we selected the AgNW network with the largest density (2.053 per $\mu$m$^2$) after 200 °C thermal annealing in order to achieve the largest TCR. However, different densities and annealing conditions could be used to meet different needs. For example, if a transparent temperature sensor is desired, the AgNW network with a lower density should be used.
To fabricate the temperature sensor, we further processed the selected AgNW network following steps (iii) to (v) as shown in Figure 4.1. Of course one question arises whether the AgNW network on glass substrate and the same AgNW network but embedded in PI have the same TCR, which will be addressed later. Kirigami, in which cuts are introduced into a 2D sheet, can transform the 2D sheet into a 3D structure. As a result, Kirigami pattern can accommodate large applied
tensile strain by out-of-plane deformation, minimizing the local strain in the sheet. Recently, the kirigami-inspired approach has been applied to develop ultra-stretchable devices. In this work, the Kirigami pattern designed had an array of straight, parallel cut lines (Figure 4.3a), with the slit length of 6 mm, slit gap of 2 mm, and beam width of 1 mm. To avoid stress concentration at the ends of the slits (i.e. crack tips), the ends were rounded with a radius of 0.2 mm. Detailed geometry design can be found in Supporting Information.

The strain sensitivity of the fabricated AgNW/PI temperature sensor was characterized. Thermoplastic polyurethane (TPU) was used to attach the two ends of the AgNW/PI sensor on a stretchable substrate by heat pressing. Then the sample was installed on a customized tensile stage, as shown in Figure 4.3a. Tensile testing was carried out while the resistance of the AgNW/PI sensor was measured simultaneously. The sensor showed outstanding resistance stability under tensile testing up to 100% strain. The variation of the resistance was within 0.05%, which was attributed to the Kirigami pattern that effectively released the local strain applied on the AgNW network. FEA simulations using Abaqus were carried out and agreed well with the experiments in terms of the deformed morphology (Figures 4.3a, b). FEA simulations showed the average tensile strain of 0.03% (with the maximum strain of 0.65%) in the loading direction, when the applied strain was 100%. Gage factor of metals is given by 1+2ν, where ν is the Poisson’s ratio. Considering that the gage factor of Ag is 1.74 (ν = 0.37), the 0.05% resistance change correlates well with the 0.03% average strain. The FEA simulations also confirmed that out-of-plane deformation is effective in reducing the local strain. Cyclic loading of 100% strain was conducted at 1 Hz and the result showed stable resistance for more than 1000 cycles (Figure 4.3c).
Table 4.1 Summary of the representative nanomaterial-enabled thermoresistive temperature sensor reported.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Sensitivity</th>
<th>Sensing Range</th>
<th>Stretchability</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT-PEDOT:PSS⁵¹⁶</td>
<td>0.61% °C⁻¹</td>
<td>22 – 48 °C</td>
<td>---</td>
</tr>
<tr>
<td>Graphene/PDMS²¹³</td>
<td>0.214 °C⁻¹</td>
<td>25 – 120 °C</td>
<td>---</td>
</tr>
<tr>
<td>CNT/PET²¹⁶</td>
<td>1% °C⁻¹</td>
<td>15 – 45 °C</td>
<td>---</td>
</tr>
<tr>
<td>Si/PDMS²¹²</td>
<td>0.71 Ω °C⁻¹</td>
<td>25 – 110 °C</td>
<td>30%</td>
</tr>
<tr>
<td>Graphene/PDMS²¹⁴</td>
<td>-1.05% °C⁻¹ @ 0% strain</td>
<td>30 - 100 °C</td>
<td>50%</td>
</tr>
<tr>
<td></td>
<td>-2.11% °C⁻¹ @ 50% strain</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuNW mesh²¹⁷</td>
<td>0.7 Ω °C⁻¹</td>
<td>RT – 48 °C</td>
<td>80%</td>
</tr>
<tr>
<td>AgNW/PI (this work)</td>
<td>0.47 Ω °C⁻¹</td>
<td>25 – 60 °C</td>
<td>100%</td>
</tr>
</tbody>
</table>

The performance of the AgNW/PI film as a stretchable temperature sensor was evaluated at the temperature range of 25 °C to 60 °C on a hot plate. A thermocouple was used to calibrate the temperature on the AgNW/PI film. The resistance of the sensor was measured under 0 % and 100 % strain. The measured resistance change ∆R/R₀ as a function of the measured temperature of the sensor is plotted for both strains in Figure 4.3d, again showing nearly no difference, consistent with the results shown in Figure 4.3c. The calculated TCR of the AgNW/PI film was 3.32×10⁻³/°C, and the sensitivity of the temperature sensor was 0.47 Ω/°C (the initial resistance of the sensor was 145 Ω). Note that for the same AgNW network with the density of 2.053 per μm² after 200 °C annealing exhibited the same TCR, either on top of the glass substrate or embedded in the PI film. The sensing performance and stretchability in this work is listed in Table 4.1, along with previously reported thermoresistive temperature sensors, for the purpose of comparison.

4.3.3. Demonstration of Wearable Temperature Sensor

The temperature sensor was applied to human body to demonstrate its general capabilities for wearable applications. Muscle temperature is a key factor during workout. Muscle temperature increases due to the metabolism during intense, dynamic exercises. Higher temperature can cause
increased fatigue and possible injuries. Our temperature sensor was attached to the biceps of a male subject to monitor the local temperatures on skin, as shown in Figure 4.4a. Skin temperature was recorded while the subject was lifting a dumbbell, in which large skin deformation was introduced to the biceps. A commercially available infrared thermometer (ANKOVO) was used to monitor the temperature at the targeted area simultaneously. The temperatures recorded from the AgNW/PI temperature sensor and infrared thermometer are plotted in Figure 4.4b. The skin temperature of the subject’s biceps was 35.3 °C before the workout, and increased up to 36.8 °C during the workout. The temperature recorded by IR thermometer before and during the workout were 35.2 °C and 36.7 °C, respectively.

Osteoarthritis is the most common chronic condition of the joints, affecting millions of people worldwide. It has been shown that patellar skin surface temperature can be used to monitor the severity of knee osteoarthritis. The temperature sensor was attached to the knee of a male subject, as shown in Figure 4.4c. Skin temperature was recorded by both the sensors and the infrared thermometer simultaneously while the subject was doing squad. The skin temperature at the subject’s knee during the squad workout was relative stable due to thin fat and muscle layer at the knee. The average temperatures recorded by the temperature sensor and infrared thermometer were 25.05 °C and 29.03 °C, respectively. The two demonstrations above illustrated that the AgNW/PI temperature sensor can monitor the subtle skin temperature change during large body deformation.
Figure 4.4 (a) AgNW/PI temperature is attached to the skin near biceps. Scale bar: 10 mm. (b) Temperature recorded by the AgNW/PI temperature sensor and infrared thermometer during biceps workout. Scale bar: 10 mm. (c) AgNW/PI temperature sensor is attached to the skin near patella. (d) Temperature recorded by the AgNW/PI temperature sensor and infrared thermometer during squad workout.
4.4. Conclusions

In summary, we report a Kirigami-inspired stretchable temperature sensor based on AgNWs for wearable applications. The sensing mechanism is based on thermoresistive effect of AgNW network embedded in PI film. TCRs of AgNW networks with different NW densities were measured. Higher AgNW density resulted in a higher TCR. Thermal annealing was found to enhance the TCR of NW films by improving the contact between NWs and removing the polymer coating around the NWs. AgNW network with the density of 2.053 per μm² after 200 °C annealing was selected to fabricate the temperature sensor, with the TCR of $3.32 \times 10^{-3}/°C$ and the sensitivity of 0.47 Ω/°C. With the designed Kirigami pattern, local strain was effectively minimized due to the out-of-plane deformation when a large tensile strain was applied. Cyclic tensile testing at 100% strain was carried out, exhibiting stable resistance over 1000 cycles. Skin temperatures at biceps and knee were monitored, illustrating the general capabilities of the AgNW-based stretchable temperature sensor for wearable applications.
4.5. Supporting Information

4.5.1. Resistance vs. Temperature

Additional resistance vs. temperature data of samples with different NW densities

Figure 4.5 Resistance vs. temperature for samples with different nanowire densities before and after different annealing temperatures.
4.5.2. Transmittance of AgNW Networks with Different Nanowire Densities

Optical transmittances of AgNW networks with different NW densities are provided for reference.

![Graph showing transmittance vs. wavelength for AgNW networks with different densities](image)

**Figure 4.6** Transmittance of the prepared AgNWs percolation network on glass slide.
4.5.3. Kirigami Pattern Design

Figure 4.7 Schematic of the designed AgNW/PI temperature sensor. $L_{\text{slit}}$ is the length of slit. $L_{\text{gap}}$ is the gap between two slits. $W_{\text{beam}}$ is the width of bending beam. $L'$ is the length of Kirigami structure. $L$ and $W$ are the length and width of sensor, respectively. Schematic of the designed AgNW/PI temperature sensor. $L_{\text{slit}}$ is the length of slit. $L_{\text{gap}}$ is the gap between two slits. $W_{\text{beam}}$ is the width of bending beam. $L'$ is the length of Kirigami structure. $L$ and $W$ are the length and width of sensor, respectively.

The designed Kirigami structure has a length $L$ of 38 mm, width $W$ of 9 mm, length of patterned region $L'$ of 18 mm and thickness $t$ of 8 μm. In the repeated pattern, the slit length $L_{\text{slit}}$ is 6 mm, slit gap $L_{\text{gap}}$ is 2 mm, beam width $W_{\text{beam}}$ is 1 mm. To avoid the stress concentration at the edge of slits, rounded edges with a radius of 0.2 mm was introduced.
4.5.4. Finite Element Analysis

3D FEA of the stretching of the PI Kirigami structure was carried out in Abaqus 6.14. The structure is $L = 38$ mm long, $W = 9$ mm wide and has a thickness $t = 8 \mu m$, in accordance with the experiments. Four-node curved shell with reduced integration elements (S4R) was used to model PI. Isotropic linear elastic behavior was assumed with Young’s modulus of 2.5 GPa and Poisson’s ratio of 0.34. The structure was subjected to 100% strain, while a small perturbation force was applied at selected nodes during the initial stages of the simulation in order to trigger out-of-plane displacement.

Figure 4.8 FEA simulation result for kirigami structure under 100% strain for (a) tilted view and (b) sideview. (c) Sideview of the kirigami structure under 100% strain.
4.5.5. Temperature Sensor Mounted on Knee

*Figure 4.9* Photograph of Kirigami temperature sensor attached to the knee during squat. The local strain at the sensor mounted area were measured to be 0%, 13.7%, 24.5% and 45.6% from left to right, respectively. Scale bar, 10 mm.
Chapter 5

Conclusions and Future Prospects

5.1 Conclusions

In summary, this dissertation investigated the applications of using AgNW as functional material to build up flexible and stretchable devices for wearable application. A new type of manufacturing approach of such devices is enabled by EHD printing, which can directly pattern high resolution and high conductivity AgNW-based patterns on various substrates.

AgNW-based flexible and stretchable touch sensors were first introduced. Capacitive touch sensors with two types of design (interdigitated and diamond-shaped) were fabricated, tested and compared. The sensors were fabricated by screen printing of AgNW percolation network on the silicon wafer, then partially embedded in a thin layer of PDMS, which is flexible and stretchable. In the design of interdigitated sensor, only one layer of AgNWs is needed (instead, diamond-shaped sensor needs two layers of AgNW), possesses the possibility of utilizing thinner design. From experimental testing and FEA simulation, the diamond-shaped sensor was proved to be more sensitive than the interdigitated one in the case of undeformed, bending and stretching. The two sensors showed robust sensitivity under tensile testing up to 15% strain. However, the sensitivity varied under bending, especially for the diamond-shaped touch cells. The sensors also showed excellent performance under cyclic loading and against oxidation. This nanomaterial enabled flexible and stretchable touch cells can be conformally attached to human body and maintain promising performance under large strain, providing a potential approach for wearable human-machine interface.

A scalable, high resolution and mask-less patterning of AgNWs using EHD printing is developed. As more promising AgNW-based functional devices have been developed by
researchers, printing techniques of AgNWs electrodes that can be applied to industry are highly demanded. This printing techniques enables direct patterning of AgNWs on a diverse range of substrates, including PDMS, PET, Glass, letter paper, nano-fiber paper, and polycarbonate filter, etc. Substrates with hydrophobic surface was treated with polydopamine to enable fine wetting of AgNW ink. High resolution (down to 45 μm) and high conductivity (up to 5.6 × 10^6 s m⁻¹) AgNW patterns are achieved by this printing technique. The printed line width was found to depend on several ink and printing parameters. Extensive parametric studies were conducted to find the optimal combination of the parameters (e.g., ink viscosity, AgNW concentration, stand-off, printing speed, voltage, nozzle size, and air pressure). Post treatment was developed to remove the binder (PEO) and enhance the conductivity. A flexible heater was developed with Peano Curve design showing a uniform temperature distribution with a maximum heating rate of ~21°C s⁻¹ and a cooling rate of ~29 s⁻¹. The patterned AgNW heater was also printed on lab-use gloves and showed stable heating performance under bending, stretching and twisting. Dry ECG electrodes with Greek Cross pattern were also printed and able to collect accurate ECG signals which is comparable with commercially available wet electrodes. This type of dry electrode is ideal for long-term wearable health monitoring.

In addition, a Kirigami-inspired stretchable temperature sensor based on AgNWs for wearable application is presented. The sensing mechanism is based on the thermoressitive effect of AgNW percolation partially embedded in thin polyimide film (~9 μm). Temperature coefficient of resistance (TCR) of AgNW percolation network with different NW densities were measured. It was found AgNW network with higher nanowire densities has a higher TCR value. Thermal annealing was also found can effectively enhance the TCR of nanowire films by improving the contacts between nanowires and removing the polymer coating around the NWs. After 200°C
annealing for 30 min, AgNW percolation network with density of 2.053 per \( \mu m^2 \) can achieve a TCR of \( 3.32 \times 10^{-3} \, ^\circ C \). And such AgNW percolation network was further processed to fabricate a temperature sensor with sensitivity of \( 0.47 \, \Omega/\circ C \). Kirigami design was utilized to make the non-stretchable AgNW/PI film to be highly stretchable. The local strain in the Kirigami pattern is effectively minimized by the out-of-plane deformation of the structure. When the applied strain is 100\%, the maximum local strain in the AgNW/PI film is only \(~0.65\%\) according to FEA simulation. Because of that, the resistance change of the AgNW/PI film could be caused by temperature change. Cyclic tensile testing at 100\% strain of the film was carried out, exhibiting stable resistance over 1000 cycles. Demonstrations of such thin-film flexible and stretchable temperature sensors were conducted by attaching the sensors on biceps and knee. The skin temperature recorded by the as-prepared temperature sensor during workout showed good correlation with the data recorded by a commercial infrared temperature sensor. This type of temperature sensor with wearable format, good sensitivity and excellent biocompatibility has the potential for long-term monitoring of body temperature.

5.2 Future Prospects

Impressive advancement has been made to develop AgNW based flexible and stretchable devices in terms of new type of sensor and its fabrication techniques. Most of the existing electronics on rigid substrates have the potential to be replaced by the AgNW-enabled flexible and stretchable electronics and find its new application in wearables. Despite the success in AgNW-based flexible and stretchable devices, there are still room to develop its new functionalities and further improve the performance of such devices, Beyond the work presented in this dissertation, the following tasks, which continue the research of this dissertation, are suggested.
Polyol method is widely used to synthesis the AgNWs due to its high yield and promising results. However, the synthesis of AgNWs with uniform diameter and length with high quality is remain a challenge. Such difference may not be a problem in the application of using AgNWs with large amount as conductors. But in the application of transparent electrode, sensors which sensing mechanism is based on material properties, printing techniques with small nozzles, high purity and uniform geometry of nanowires are preferred. Moreover, nanowire with larger diameter are found causing haze in transparent application. Longer nanowire are preferred to effectively build connections with low densities according to percolation theory. In addition, a layer of PVP is coated on the surface of nanowires due to the synthesis processing. Such PVP layers can be removed by washing the as-prepared nanowires in acetone. However, a large number of nanowires are wasted in this tedious process. A more efficient approach of post treatment after nanowire synthesis is needed.

Touch sensing is promising input in human-machine interface. Developing large area, transparent, highly sensitivity, skin-like touch panels is of important in development of next generation of wearable touch screens. Coating of transparent electrodes with AgNWs has been realized by spray coating, spin coating and Meyer-rod coating. But patterning transparent AgNW conductors is challenging in terms of low material consumption, large area, high resolution, and good uniformity. Hence, a new AgNW patterning technique for such application needs to be developed. Additionally, the shape of the touch cells can be further improved by introducing small features. Improvements in the sensitivity and performance under large deformation can be achieved by modifying the design of touch cells.

EHD printing enables direct printing of high resolution and high conductivity AgNW patterns, providing a promising approach to pattern on various substrates. Currently, the printed
AgNW are 2D patterns and only being used as conductors. 3D conductive structures might be printed by changing the formula of AgNW ink. And by carefully engineering the design of printed 3D structures, ultra-stretchable and interesting structures could be fabricated (e.g., kirigami, auxetics). Here, the AgNW should be uniformly dispersed in a fast-dry, polymer-based ink with high viscosity. To realize good dispersion of AgNWs in ink, chemical treatments to the AgNWs may be need (e.g., ligand exchange). Additionally, the printed structure should be highly conductive after printed, no posttreatment is required.

Smart structures (e.g., wavy structures, origami and kirigami, etc.) add stretchability to non-stretchable materials, providing an alternative way to develop ultra-stretchable electronics for wearable applications. The mechanics of such structures should be studied to have a better understanding of the structures, in order to assist the design of such structures (e.g., 2D stretchable kirigami structure). Moreover, EHD printing and smart structure could be combined by printing functional materials at selected region of the smart structures. For instance, printed heater at joint/crease of a origami structure made of shape memory polymers (SMPs), printed conductive traces at the beam in kirigami structures.

With more AgNW based electronics has been developed, the fundamental properties of AgNW/polymer composites need to be characterized. As AgNW is a high aspect ratio 1D material, anisotropic effect is expected. For instance, thermal conductivity of AgNW/PDMS composite in in-plane direction and out-of-plane direction, thermal expansion of aligned AgNW/PI composite in two different directions, etc. Such fundamental properties are essential for developing AgNW-based electrode for wearable applications.
REFERENCES


