Selective Deposition of Metallic and Semiconductor Materials onto DNA Templates for Nanofabrication

Jianfei Liu
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Selective Deposition of Metallic and Semiconductor Materials
onto DNA Templates for Nanofabrication

Jianfei Liu

A dissertation submitted to the faculty of
Brigham Young University
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

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December 2011

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ABSTRACT

Selective Deposition of Metallic and Semiconductor Materials onto DNA Templates for Nanofabrication

Jianfei Liu
Department of Chemical Engineering
Doctor of Philosophy

This work examines the selective deposition of metallic and semiconductor materials onto DNA templates for the fabrication of nanodevices. DNA origami provides a simple and robust method for folding DNA into a variety of shapes and patterns and makes it possible to create the complex templates needed for nanodevices, such as nanoelectronic circuits, plasmonics, and nanosensors. Metallization of DNA origami templates is essential for the fabrication of such nanodevices. In addition, selective deposition of semiconductor materials onto the DNA template is of importance for making many nanodevices such as nanocircuits.

Metallization of DNA origami presents several challenges beyond those associated with the metallization of other DNA templates such as λ-DNA. All of these challenges were addressed in this study. DNA origami templates were seeded with Ag and then plated with Au via electroless deposition. Selective continuous metal deposition was achieved, with an average metallized height as small as 32 nm. The structure of T-shaped DNA origami was also retained after metallization. Following the metallization of complete origami, site-specific metallization of branched DNA origami was also demonstrated. To achieve this, staple strands at select locations on origami were replaced with staple strands modified with binding sites at the end. These binding sites then attached to thiolated DNA coated Au nanoparticles through base pairing. The continuous Au nanowires formed at designated sites on DNA origami after Au plating had an average width of 33 nm, with the smallest ones ~20 nm wide. The continuity of nanowires was verified by conductivity tests- the only tests of this nature of which I am aware. Moreover, predesigned sites on “circuit-shaped” DNA origami were successfully metallized.

The selective deposition of a variety of materials onto DNA templates for the formation of continuous DNA-templated nanowires was also demonstrated. Specifically, an electroless Ni plating solution was developed to enable the fabrication of uniform and continuous DNA-templated Ni nanowires. Tests showed that these DNA-templated Ni nanowires were conductive. Moreover, continuous DNA-templated Bi$_2$Te$_3$ and/or Te nanowires have been fabricated through galvanic displacement of DNA-templated Ni and Cu nanowires. Altogether, these results represent important progress toward the realization of DNA-templated nanofabrication.
Keywords: Jianfei Liu, DNA origami, metallization, electroless plating, nanowire, site-specific, nickel, gold, silver, copper, semiconductor, tellurium, bismuth telluride, conductivity test, nanocircuits
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1 INTRODUCTION

Integrated circuits have achieved remarkable increases in speed and density over the last two decades. In spite of this, the desire for such increases remains unsatisfied. While current fabrication methods appear adequate to meet demands in the near term, a transformative method that overcomes the limitations inherent in today's semiconductor fabrication methods would aid in meeting long-term needs. Bottom-up nanotechnology, which utilizes the recognition properties of molecules to self-assemble and form nanostructures [1], provides an alternative fabrication path for future generation nanoelectronic circuits. The combination of top-down and bottom-up nanotechnology could simultaneously address the limitations of throughput, cost and resolution that prevent large-scale fabrication of integrated circuits and sensor elements with features sizes near 10 nm.

The present work is part of efforts at BYU to develop novel, scalable processes for nanocircuit fabrication to meet future demands by taking advantage of both bottom-up self-assembly and top-down patterning. That effort focuses on the development and refinement of four key technologies (see Figure 1-1): (1) solution-phase assembly of DNA templates, (2) high-resolution surface patterning, (3) high-precision metallization of DNA templates, and (4) chemically directed assembly and integration of nanostructures on surfaces [2, 3]. The research has a potential to bring revolutionary changes to the electronics industry and substantial benefits
to society. The technology developed in this research could also be used for plasmonic applications \[4, 5\].

Figure 1-I. Molecular circuit assembly and wiring. (A) MC template is formed in solution using DNA origami. (B) A surface is chemically patterned to direct MC assembly. (C) DNA origami is aligned and attached to the surface. (D) Site-specific metallization of the DNA origami. (E) Localization of active components to the DNA origami.

In this work, DNA molecules are used as templates for nanoelectronic circuits. DNA is an attractive template for the directed self-assembly of nanometer scale structures because of its size, flexible backbone, self-recognizable base pairs and arbitrary designable length and sequence \[6\]. This work is primarily on selective metallization of these molecular templates. Metal is deposited at designated sites on DNA templates to create nanowires, leaving other sites
for the local deposition of, for example, semiconductors that serve as active elements for nanocircuits.

Recently, a method was developed to fold long, single stranded DNA (scaffold strand) into arbitrary shapes by using numerous short single DNA strands (staple strands) for direction and as stabilizers. The method [7] was named “scaffolded DNA origami,” and is frequently referred to as just “DNA origami.” Compared to other forms of DNA (i.e. double-stranded DNA), DNA origami offers a robust route to make templates that provide the increased complexity for a variety of applications, such as nanoelectronics and plasmonics [7, 8]. The metallization of DNA origami, however, presents some challenges not present in other DNA templates that have previously been metallized. Moreover, the metallization of specific areas of DNA origami is a significant challenge that must be overcome to enable nanoelectronic circuit fabrication. This work demonstrates our efforts to address all of these challenges to realize the selective metallization of both the whole structure and specific areas of DNA origami templates. This work on the metallization of DNA origami represents significant progress toward the realization of DNA-templated nanocircuits.

Use of DNA templates for device fabrication requires the ability to deposit materials other than just metals. Deposition of semiconductor materials onto DNA templates has been studied since 1996 [9]. However, there are several challenges related to semiconductor deposition that must be addressed to enable the fabrication of DNA-templated nanoelectronic circuits. In this work, these challenges are addressed through use of galvanic displacement to selectively deposit semiconductor materials onto DNA templates.
Scope of the Project

Prior to this work, the metallization of DNA origami had not been demonstrated. Experimental demonstration of selective metallization of entire DNA origami structures and site-specific metallization of DNA origami is the primary objective of this study. Techniques to selectively deposit other materials are also examined. This work describes my efforts to understand and address challenges related to the use of DNA origami templates for nanoelectronic circuits and other nanodevices.

Outline

Background. Chapter 2 discusses the background for nanofabrication, basic properties of DNA related to nanofabrication, deposition of metallic and semiconductor materials on DNA. Opportunities related to the DNA-templated nanofabrication are summarized.

Metallization of branched DNA origami for nanoelectronic circuit fabrication. Chapter 3 discusses the challenges on metallization of complete DNA origami structures. The efforts for addressing these challenges toward the successful metallization of complete DNA origami structures were also presented.

Site-specific metallization of DNA origami for nanoelectronic circuit fabrication. Chapter 4 describes my efforts for the successful metallization of DNA origami at predesigned locations. The processes for the successful metallization of T-shaped DNA origami and circuit-shaped DNA origami at specific locations are presented.

Fabrication of continuous DNA-templated nickel and copper nanowires and galvanic displacement of them by tellurium and bismuth telluride. Chapter 5 describes the fabrication of...
Conductive DNA-templated Ni nanowires and continuous DNA-templated Cu nanowires. A new electroless Ni plating solution was developed to fabricate conductive Ni nanowires. Moreover, it shows my processes to fabricate DNA-templated Te and/or Bi₂Te₃ nanowires through the galvanic displacement DNA-templated Ni and Cu nanowires.

Conclusions and future work. Chapter 6 presents the summary of this work. Future opportunities based on the work presented in this dissertation are also described.
2 BACKGROUND

2.1 Top-down and Bottom-up Technology

A typical electronic circuit consists of multiple components, such as transistors and diodes, connected electronically by metal wires. Transistors are active components that utilize semiconductor materials. The ultimate goals of this research are to achieve site-specific metallization of DNA origami templates and to explore techniques for local deposition of additional materials on these same templates in order to enable nanoelectronic circuit development with bottom-up techniques.

2.1.1 Top-down Technology for the Fabrication of Nanoelectronic Circuits

Conventional top down technology is widely used in semiconductor device fabrication. It consists of multiple photolithographic and chemical treatment processes (hundreds of steps) on a silicon wafer by which the electronic circuits are gradually fabricated. The size-resolution of the technology is heavily dependent on the wavelength of the light in use. With the progress of facilities and technology, the photolithography approach is able to create features smaller than 100 nm. Currently, the industry has demonstrated the feasibility of 22 nm, and is working towards production at that level [10]. However, there are significant challenges for lithographic technology at feature sizes below 22 nm [11]. It may be possible to use X-rays, electron-beams
or ion-beams, which can create features as small as 10 nm [12], for top-down fabrication. However, limitations of materials, throughput, and cost prevent these techniques from being used for integrated circuit manufacturing in industry. Recently, some novel AFM-based top-down nanolithography technologies have been developed, such as chemomechanical patterning, dip pen nanolithography, AFM mechanical scribing and nanoidenting, and c-AFM oxidation [13-17]. Although these AFM based techniques can go to as small as 10 nm, they also suffer from the cost and throughput limitations.

2.1.2 ‘Bottom-up’ Nanotechnology

In contrast to ‘top-down’ technology, ‘bottom-up’ nanotechnology utilizes the recognition properties of single molecules to self-assemble and form useful nanostructures [1]. Bottom-up nanotechnology provides an alternative path for nanofabrication, a potential way of simultaneously addressing the problems of cost, throughput, and resolution.

DNA is an ideal scaffold material for 'bottom-up' construction of nanoelectronic circuits because of its nanoscale size, arbitrary long length, designable sequences, self-recognizable base pairs and flexible backbone [6]. In 2006, Rothemund successfully created different nanoscale shapes and patterns by folding DNA using ‘DNA origami’ [7]. This provided a convenient method to fold DNA into patterns for nanoelectronic circuit templates. As the conductance of DNA is very sensitive to the experimental parameters [18], it cannot be used as either conducting wires or as active components of electronic circuits. Consequently, metals and semiconducting materials will be localized onto DNA templates to function as wires and active components for nanoelectronic circuits.
2.2 Basic Properties of DNA

2.2.1 DNA Double-Helix Structure

Watson and Crick revealed and investigated the double helix structure DNA (deoxyribonucleic acid) in 1953 [19, 20]. DNA consists of aromatic bases, pentose sugars, and phosphate groups. The four bases found in DNA are adenine (A), guanine (G), thymine (T) and cytosine(C). In the DNA double helix, A on one strand only interacts with T on the other strand, while G on one strand only interacts with C on the other strand. These special interactions, which hold the two strands together, are named complementary base pairing. These interactions are caused by hydrogen bonds formed between bases. These hydrogen bonds are formed between a covalently bound, positively charged H atom and a negatively charged carbonyl oxygen or nitrogen [21]. There are two hydrogen bonds that are separated by 2.82 and 2.91 Angstroms in A–T base pair [22], while there are three hydrogen bonds in G–C base pair that are separated by 2.84-2.92 Angstroms [23].

Another important concept about DNA is axial rise, which is the distance between adjacent planar bases in DNA double helix. For B-form DNA, which has right-handed double helix structure, this value is about 3.4 Angstroms. This small distance provides the possibility of localization of foreign materials or additional functional groups onto DNA with high density. The B-form DNA has a diameter of 20 Angstroms (see Figure 2-1). The small diameter of DNA molecule is one of the important reasons why I use it as the template for nanoelectronic circuits.
2.2.2 Physical Properties of Double-stranded DNA

Double-stranded DNA is stable due to the hydrogen bonding and base stacking interactions. In addition, water molecules, which form a “shell of hydration” around DNA by solvation or covering, help to stabilize DNA. However, double-stranded DNA unwinds and separates into two single strands at pH>12 or pH<2 because of the ionization of bases. Increased
temperature also destabilizes the double helix as both the hydrogen bonds and the shell of hydration will be destroyed when the vibrations become stronger than the interaction [21].

In addition, DNA adsorbs ultraviolet (UV) light at 260 nm. This property can be used for checking the concentration and purity of DNA. Moreover, it can be utilized as the evidence for the reaction between DNA and other materials.

**Electrostatic Forces in DNA**

DNA, in both a helical and a randomly coiled structure, is a polyelectrolyte due to the series of phosphate groups on its backbone. Because of the high concentration of negative charge on DNA, electrostatic interactions play an important role in DNA function.

Manning’s counter ion condensation theory provides a prediction of the total fraction of polyion charge on DNA neutralized by a single ion species [25, 26]. However, it does not provide the distribution of counter ions adjacent to DNA. The experimental detection of ion distributions around DNA is very difficult. Instead, the Poisson-Boltzmann equations, Monte-Carlo (MC) simulations and Molecular Dynamics (MD) simulations have been used to find the spatial distribution of charge density around DNA [27-29].

Cation exchange can take place on the DNA phosphate backbone. A typical DNA solution consists of DNA molecules and buffer solutions that are composed of cations such as Na\(^+\) and/ or Mg\(^{2+}\) and organic anions. The cation-exchange processes on DNA have been modeled with the use of Poisson-Boltzmann analysis, MC simulations [30], and MD simulations [29]. The competitive association of DNA and different cations due to electrostatic interactions is described as D, the analog of an equilibrium constant for the ion exchange reaction. Previous MC simulation results by Record et al. [30] showed that D was relatively independent of the bulk
ion concentrations. MC simulations also showed that \( \ln D \) exhibited a linear relationship with the ratio of radii of the competing cations [30]. Lyubartsev et al. used a combination of MC simulations and MD simulations to calculate the relative binding affinities of different alkali ions to DNA [29]. The resulting binding affinities of alkali ions to DNA were as follows: \( \text{Cs}^+ > \text{Li}^+ > \text{Na}^+ > \approx \text{K}^+ \) [29].

**Chemical Attachment to DNA**

Results from laser Raman spectroscopy by Duguid et al. show that divalent transition metal cations (\( \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Pd}^{2+}, \text{Cd}^{2+} \)) have specific metal interactions with acceptor sites on the purine (N7) and pyrimidine (N3) rings [31], in addition to the electrostatic interactions mentioned above. Their interactions with DNA bases are much stronger than with DNA phosphates, except for \( \text{Cu}^{2+} \), which strongly perturbs both base and phosphate group vibrations. In contrast, alkaline earth elements show stronger affinities for phosphates. Metal cations with very strong base affinity can disturb the hydrogen bonding and destabilize the B-form of DNA. Studies from other groups using different techniques show that metal ions bind preferentially to the bases relative to phosphates in the following order: \( \text{Hg}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+} > \text{Ni}^{2+}, \text{Co}^{2+} > \text{Fe}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} \) [31]. The interactions between metals and DNA bases represent an important aspect of metallization.

**DNA Self-assembly**

The rules of complementary base pairing show that each type of base on one single DNA strand forms bonds with only one type of base on the other single DNA strand. That is, A only bonds to T while C only bonds to G on DNA. Typically, only when all bases on one strand are
complementary with those on the other strand, the two strands bind together and form double-stranded DNA. In 1982, Seeman [32] proposed that simple junction structures (i.e. Y) could be prepared from DNA. He believed that these individual DNA junction structures could then be assembled into complex DNA structures with single-stranded DNA segments through base pairing [32]. Since then, researchers developed different methods to assemble DNA into nanostructures. A significant breakthrough in the field happened in 2006, when Rothemund [7] developed ‘DNA origami’ (see Chapter 1 for the definition). Using this technique, a variety of folded DNA structures was assembled. In his article, Rothemund presented the formation of six different 2-D structures self-assembled using DNA, as shown in Figure 2-2 [7]. Later, Shih’s group expanded this method to construct 3-D nanostructures by constraining pleated layers of helices to a honeycomb lattice [33]. It took more than a week to fold these 3-D DNA origami nanostructures. Recently, Yan et al. developed a method to fold 3-D DNA origami with complex curvatures [Figure 2-3] [34]. DNA origami is dynamic structure when exposed to solution and is always unfolding and folding. Compared to λ-DNA, DNA origami is less stable since the unfolding between short staple strands and the main scaffold of DNA origami is easier than that between two long single strands of λ-DNA. This unfolding can change the shape of DNA origami. Despite the disadvantages, DNA origami also provides important advantages that don’t apply to λ-DNA. For instance, staple strands can be adjusted to create attachment points at designed places throughout the origami structure. This can be done either by direct chemical modification at the ends of staple strands or by extending staple strands with additional nucleotides and hybridizing with a complementary sequence containing the desired functional group or moiety being attached. Thus, ‘DNA origami’ not only offers a route of making complex
templates needed for nanoelectronic circuits, but also provides opportunities of creating attachment points for localization of other functional groups and materials [35].

Figure 2-2. DNA origami shapes (reproduced with permission from [7]; Copyright 2006, Macmillan Publishers Ltd.)

Figure 2-3. Design and folding of 3-D DNA origami with complex curvatures (reproduced with permission from [34]; Copyright 2011, American Association for the Advancement of Science)

2.3 Metallization of DNA Templates

The conductance of DNA itself is very sensitive to experimental parameters and cannot be used as wires for nanoelectronic circuits [18]. In 1998, Braun et al. [36] reported a method of fabricating continuous nanowires on the DNA template through seeding and electroless plating. They put Ag seeds onto λ-DNA, then enlarged and connected the seeds using electroless Ag plating to form continuous Ag nanowires. Since then, this seeding and electroless plating method has been adopted by many groups as the method for preparing DNA-templated metal nanowires.
During the last 13 years, different methods have been explored in the literature to put metal seeds onto DNA, as described below in detail. Besides this seeding and electroless plating method, there are some other methods reported for DNA metallization, which include 1) slowly depositing a compound (e.g. PdO) containing the metal element of interest onto DNA for a long period of time to form continuous compound nanowires and then reduce the compound to obtain metal nanowires [37], 2) forming and growing metal deposits on the DNA template in the presence of metal ion and microwave or UV light [38].

To finally form DNA-templated nanoelectronic circuits, metal should be deposited onto designated locations on DNA, leaving other areas of the template for active components such as semiconducting carbon nanotubes, elemental and compound semiconductors. The deposition of metal at designated locations of DNA is called site-specific metallization of DNA.

2.3.1 Seeding and Electroless Plating

Electroless Plating

Electroless plating is usually used to describe three fundamentally different types of chemical plating carried out without the use of a power supply: (a) galvanic displacement, (b) autocatalytic processes, and (c) substrate-catalyzed processes [39]. Electroless plating is highly attractive for achieving desired plating because of its simplicity, which requires no external power supply and no elaborate equipment. The term “electroless plating” is frequently used synonymously with autocatalytic plating [40], and will be used that way in the balance of this dissertation. In autocatalytic plating, the metal substrate (catalyst for plating) is immersed in an aqueous solution and the reaction takes place immediately, depositing metal on the substrate. The deposited metal layer then catalyzes the subsequent reaction so that the plating continues
Therefore, autocatalytic plating is not self-limiting. As long as the plating solution is not depleted and the plating conditions are not changed, the plating on the catalyst will continue.

Electroless plating of cobalt, chromium, copper, gold, iron, nickel, palladium, platinum, silver and vanadium has been demonstrated in the literature [39, 41]. An electroless plating bath consists of metal ions, a complexing agent, a buffer (the complexing agent can also serve as the buffer), a reducing agent, and sometimes additives and a stabilizer. Additives such as an accelerator and/or an inhibitor are in use in some plating solutions for particular purposes [40]. For instance, polyethylene glycol (PEG) was added into an electroless Cu plating solution as an inhibitor in order to enable filling of trenches to fabricate Cu interconnects for the ultra-large-scale integration of electronic circuits [42].

Although electroless plating does not require an external power supply, a catalyst for the reaction is required. Transition metals often function as catalysts for electroless plating. The catalyzing effect of metals (Figure 2-4) on both the anodic and cathodic plating reactions is due to the inner orbital vacancies in their atomic structures. This is why the catalysts for electroless plating are usually transition metals. In the plating process, molecules or atoms of the reducing agent chemisorb and bind to the metal catalyst by donating electrons to the orbital vacancies [41]. These donated electrons then reduce metal cations adsorbed on the catalytic surface so that the metal deposition takes places on the catalyst. The initial catalyst needs to be conducting, but it does not need to be the metal to be plated. But, after the initial plating, the metal plated needs to be able to act as the catalyst so that the electroless plating can continue.
Other basic requirements for electroless plating of a particular metal are: (1) the reduction potential must be high enough so that the reaction with the chemical reductant can occur, (2) the reduction of the metal must occur preferentially to water decomposition, and (3) the metal deposited on the surface must be able to catalyze the plating reaction. In addition, the activation energy of the autocatalytic reaction must be low enough that the reaction can occur below the boiling point of the solution [41].

Selectivity of plating is defined as the ratio of the plating that takes place on the desired catalyst-activated sites to that which takes place over the entire surface. Good selectivity requires the plating to take place totally or mostly on the catalyst-activated sites. Metal deposits preferentially on the catalyst surface, rather than in the bulk solution because the former path provides a lower activation energy [41]. Thermodynamically, an electroless plating solution is an unstable system. Given a certain amount of time, the electroless plating solution will nucleate spontaneously in a homogeneous fashion and plate without the presence of catalyst. Depending on the bath composition and temperature, the solution may be stable for a few minutes, hours, days, or months. If plating occurs without a catalyst, it will cause non-specific deposition and
impact negatively the selectivity of plating. A complexing agent, which forms a stable complex with the metal ion, is used to enhance the stability of metal ions and hence the selectivity of the plating.

An understanding of the mechanism by which electroless plating occurs is important since I need to manipulate the plating to achieve the desired metal deposition. Mixed-potential theory has been successfully applied and verified for the electroless deposition of Cu, Au, and Ni [43]. It can be applied to this research for the analysis of electroless plating of Cu and Ni. The overall reaction that takes place during electroless metal deposition is

$$\text{M}^{z+} + \text{Red} \rightarrow \text{M} + \text{Ox}, \quad (2-1)$$

in which Red is the reducing agent and Ox is the oxidation product of the reaction. The mixed-potential theory [39, 44-46] of electroless plating divides reaction 2.1 into a reduction or cathodic reaction

$$\text{M}^{z+} + ze^{-} \rightarrow \text{M}, \quad (2-2)$$

in which complexed metal ions are reduced, and an oxidation or anodic reaction

$$\text{Red} \rightarrow \text{Ox} + ne^{-}. \quad (2-3)$$

In order to have the overall reaction occur, the free energy change must be negative. Since

$$\Delta G = -nFE, \quad (2-4)$$

E needs to be positive to have the reaction take place. E, the equilibrium potential of the overall reaction, can be calculated through the following equation:

$$E = E_C - E_A. \quad (2-5)$$
in which $E_C$ is the electrode potential of cathodic reaction and $E_A$ is the electrode potential of anodic reaction, relative to a standard hydrogen electrode.

During electroless plating, since both cathodic and anodic reactions take place on the same catalytic, conducting metal surface, both reactions occur at the same electrode potential. In other words, a mixed potential (V) [39, 45, 46] is reached during the plating. Since the plating takes place by transferring electrons from the reducing agent to the metal, the cathodic and anodic reaction rates are equal to each other at steady state. In the beginning of reaction, it’s possible that the rates of cathodic reaction and anodic reaction are different. For example, if the anodic reaction is faster at the beginning, the build-up of electrons will then change the potential of the catalyst, which will slow down the anodic reaction and accelerate the cathodic reaction until both reaction rates are equal. The understanding of mixed-potential theory can help me manipulate the electroless plating bath to achieve desired metal deposition. For instance, to change the rate of the electroless plating, I could change the mixed-potential through changing the concentration of reactants.

In this research, electroless plating will be used to facilitate the selective growth of metal seeds to form continuous nanowires on λ-DNA and DNA origami templates. In order to obtain selective plating, a complexing agent will be used to stabilize the solution so that homogeneous plating will not take place in solution. More importantly, to achieve the desired plating, I can manipulate the half-cell reactions by changing parameters such as the concentration of metal ions and reducing agent, the complexing agent, and the pH.
Seeding of DNA

As mentioned above, transition metals are needed to catalyze electroless plating reactions. However, there is no transition metal present on natural DNA. Therefore, a process was developed to form transition metal nanoparticles on the DNA template. This process is called seeding. The selectivity of seeding is defined according to the ratio of seeds deposited onto the DNA to those deposited on the entire surface or rest of the surface. Good selectivity requires the seeds to be formed only or mostly on the DNA, with little or no seeding of the background substrate. Moreover, to form DNA-templated nanoelectronic circuits, the seeds need to be localized to designated areas on the DNA template, which is called site-specific seeding.

One method of seeding involves the electrostatic interaction between the negatively charged DNA backbone and positively charged metal colloids or metal cations [36, 47-56]. Ongaro et al. [51] used 4-(dimethylamino) pyridine (DMAP)-modified, positively charged gold nanoparticles to seed DNA through the interaction with negatively charged phosphate groups on the DNA backbone. Richter et al. [52, 53] used Pd$^{2+}$ to interact with DNA and formed Pd nanowires. However, non-selective deposition of Pd on the substrate surface was also significant in work by Richter et al. Braun et al. [36, 47] seeded DNA with [Ag(NH$_3$)$_2$]$^+$, during which [Ag(NH$_3$)$_2$]$^+$ attaches to the negatively charged DNA through an ion exchange reaction and by forming complexes with the DNA bases. Silver ions attached to DNA were then reduced to metallic Ag nanoparticles in a separate step. This Ag seeding method is relatively selective, probably due to the much stronger interaction between [Ag(NH$_3$)$_2$]$^+$ and DNA than that between [Ag(NH$_3$)$_2$]$^+$ and the surface. Thus, different ions and charged nanoparticles can be used to seed
DNA through electrostatic interaction with the DNA backbone. The selectivity of seeding is different, depending on the specific ions, as discussed in Section 2.2.2.

A second seeding method is based on complex formation between metal ions and the nitrogen groups on DNA bases [57-62]. Pt(II) and Pd(II) form strong complexes with the N7 atoms of the bases guanine and adenine. Pd(II) also has a strong interaction with the N3 atoms of the bases thymine and cytosine (see Figure 2-1) [63]. Palladium ([PdCl₄]²⁻) and platinum tetrachloro anions ([PtCl₄]²⁻) can form PdCl₂(H₂O)₂ and PtCl₂(H₂O)₂ after hydrolysis in water, which then bind to the bases on DNA [62]. Gu et al. [58-60] used both [PdCl₄]²⁻ and [PtCl₄]²⁻ while Mertig et al. [61, 62] used [PtCl₄]²⁻ to interact with DNA. The palladium or platinum ions binding to DNA were then reduced in a separate step by reducing agents such as dimethylaminoborane (DMAB) to form metallic seeds [58-62]. Cis-diamminedichloroplatinum, which can hydrolyze and form a covalent bond with the electron pair “donor” atoms such as the N7 atoms of the purine nucleotides, was also used to seed DNA [57]. Seeding through the formation of a complex between palladium or platinum ions and the DNA yielded seeds that were neither uniform nor continuous with diameters between 1 and 6 nm [58-62]. The selectivity of seeding by this method was not very good since metal ions also attached to and seeded the substrate surface [58-62].

In a third way of DNA seeding, DNA can be chemically modified to enable deposition of metal nanoparticles for seeding. Glutaraldehyde (GA) was used to modify DNA, as one of two aldehyde groups can react with and attach to the amino groups on cytosine and guanine in DNA [64, 65], while the other aldehyde group added onto DNA can be used to reduce two silver ions to form silver seeds. This seeding method is called the GA method in this dissertation. The GA method was developed by Keren et al. and improved by Park et al [66-72]. Keren et al. deposited
GA-modified DNA onto a surface, then seeded DNA on the surface overnight and obtained continuous nanowires with relatively good selectivity after subsequent plating. Park et al. seeded DNA in solution for 30 min after GA modification and obtained continuous nanowires with very good selectivity after plating. Their results achieved by seeding in solution appeared to provide better selectivity, probably by avoiding the interaction between metal ions and the substrate surface. Using GA to modify DNA, site-specific seeding of DNA was achieved by Keren et al. through two methods: (1) selectively covering a specific sequence of DNA with a protein and seeding the unprotected portions [66, 67]; and (2) reacting selected, single-stranded DNA with GA before hybridizing it with a complementary strand to form double-stranded DNA [72]. In another approach, Simon et al. used artificially modified, double-stranded DNA to facilitate metal binding with DNA [73]. They incorporated alkyne-modified cytosine into the polymerase chain reaction (PCR) fragments. Afterwards, the alkyne groups were converted into sugar triazole products through click chemistry, which were then reacted with Tollens reagent (silver ammonia solution) to obtain silver seeds on DNA [73]. However, their work did not result in continuous nanowires or nanorods. Thus, by chemically modifying DNA, the entire or the specific parts of DNA can be seeded. The continuity of resulted nanowires after plating depends on the chemicals and processes used for DNA modification.

As discussed earlier, site-specific seeding of DNA is needed for the fabrication of DNA-templated nanoelectronic circuits. Site-specific seeding could be achieved in the following two ways: (1) seeds should have interaction with specific sequence or bases if DNA is not modified; or (2) only specific locations of DNA should be modified with binding sites for seed localization. Prior to the start of current study, Keren et al. were the only investigators to demonstrate site-specific seeding of DNA, which was achieved on double-stranded DNA with use of the GA
method [66, 67, 72]. The success of this method for site-specific seeding was because the reaction between DNA and GA to add aldehyde groups in order to create binding sites at specific locations did not impact the hybridization of the DNA. To date, there has been no report of successful, site-specific seeding of DNA through electrostatic interactions or complex formation. This is due to the fact that metal ions or NPs cannot interact with either specific DNA sequences or with specific bases. Site-specific seeding may be achieved by attaching metal ions or colloids to selected, single-stranded DNA through electrostatic force or the formation of a complex, and then assembling the single stranded DNA to form the desired DNA structure.

As discussed in Section 2.2, DNA origami provides the opportunity to create specific binding sites throughout origami structure by extending the staple strands. For instance, a possible site-specific seeding method is to attach single-stranded DNA to a Au or Ag nanoparticle through a thiol-metal interaction, and then use these strands to attach the nanoparticle to a complementary strand (binding site) on the targeted DNA template. The Au/Ag nanoparticles would then serve as the seeds for subsequent plating. There are several examples in the literature of sequence specific attachment of nanoparticles to self-assembled DNA templates using this approach. Attachment of Au nanoparticles to DNA using this method was first demonstrated by Le et al. in 2004 [74]. In that work, DNA scaffolding (not DNA origami) was assembled in solution and deposited onto a mica surface. Au nanoparticles with multiple, identical single DNA strands (complementary to those on the self-assembled DNA template) were deposited onto the surface. Because of DNA hybridization, Au nanoparticles of uniform diameter were deposited onto designated locations on the self-assembled DNA to form Au-nanoparticle arrays. In studies parallel to this work, Hung et al. [75] used the same approach to localize Au nanoparticles onto lithographically confined triangular DNA origami on a silicon
dioxide surface in 2009; in 2010, Pal et al. [76] localized both Au and Ag nanoparticles onto triangular DNA origami, expanding the materials that can be patterned onto DNA origami. In another study parallel with this work, Pais et al [77] plated Ag on Au NPs attached to selected locations on 100 nm x 100 nm DNA origami tile in 2011. There was no report on plating on the Au or Ag nanoparticle-patterned DNA origami prior to the start of my study.

To conclude, different methods have been developed for the successful seeding of DNA, including the use of electrostatic interactions, complex formation and chemical modification. Of all these seeding methods, only the GA method has led to highly selective seeding of double-stranded λ-DNA. Site-specific attachment of particles has been demonstrated recently and can be accomplished with DNA origami by adjusting staple strands for localization of functional groups or binding sites. Such particles should be useful as seeds for subsequent metal deposition at specific sites.

### 2.3.2 Other Methods for Metallization of DNA Templates

Nguyen et al.[37] selectively and slowly deposited polar PdO, which was formed by the hydrolysis of $\text{PdCl}_4^{2-}$, onto DNA by electrostatic force. The whole hydrolysis process and seeding process took about two weeks. Continuous PdO nanowires were finally formed on λ-DNA and reduced to obtain metallic Pd nanowires. The diameter of continuous Pd nanowires prepared was as small as 25 nm [37]. However, the long time needed for the whole process is a significant drawback of this metallization method. This process may not be used for metallization of DNA origami since DNA origami would likely unfold and lose its structure during such a long period of time in metal solution.

Recently, Kundu et al. reported that the hydroxyl group (in the deoxyribose) of DNA molecules, in the presence of microwave heating, can initiate the reduction of Au (III) onto DNA
to form Au seeds. The seeds grew to continuous nanowires with diameters about 12-15 nm during the microwave heating processes. The concentrations of DNA and Au ions, as well as the time for microwave heating, were essential for the formation of continuous DNA-templated nanowires using this microwave method [44]. It was necessary to control the ratio of metal ion concentration to DNA base concentration to a value between 2 and 3 to form nanowires. No particles were formed on DNA at a smaller ratio (0.5) and larger particles (25-30 nm) were formed at a larger ratio (5). At the larger ratio, there was no evidence to demonstrate unequivocally that the large particles were formed on the DNA, although that appeared to be the case. Non-specific deposition (deposition in solution or on the background) was significant, which might restrict the method from being used for metallization of small DNA such as DNA origami. Due to the limited concentration of Au ions in the solution, only a small fraction of the DNA was metallized, resulting in a low yield. The mechanism that determines the formation of nanowires from individually separated seeds is not well understood. The same group [78] also reported the formation of DNA-templated Pd nanowires by exposing DNA and Pd ions in solution to ultra violet photoirradiation. Similar to the microwave method, the ratio of metal ion concentration to DNA base concentration was controlled to a value between 1 and 3 to form nanowires. The average diameter of these nanowires was about 55 to 75 nm. Due to the limited Pd ion source in solution, only a small percent of DNA were metallized. This low yield from the microwave and UV methods and the lack of selectivity prevented these methods from being used in the current study.
2.3.3 Metallization of DNA Templates with Ni

Ni is a magnetic material. Ni nanowires are potential materials for applications in high-density information storage [79]. Ni is also an active metal, so that the fabrication of Ni nanowires on DNA templates provides the opportunity for the deposition of a variety of other materials onto DNA. Preparation of DNA-templated Ni nanowires has been reported in the literature Ni [60, 80]. However, conductive DNA-templated Ni nanowires with a uniform size have never been demonstrated [60, 80].

2.3.4 Metallization of DNA Origami

Although most research on DNA metallization in the literature was done on λ-DNA templates, a few other types of DNA templates have been used for metallization. Harnack et al. [81], Fischler et al. [73], Yan et al. [71], Park et al. [69], and Pais et al. [77] used calf thymus DNA, artificial DNA, self-assembled DNA nanoribbons, three-helix bundles, and DNA origami tiles for the DNA metallization, respectively. However, there was no report of continuous metallization of DNA origami prior to the present study. All other researchers who worked on the metallization of DNA have used λ-DNA as a template. There are three reasons why λ-DNA is so frequently selected for metallization. First, it is easy to locate under AFM, SEM, STM, and TEM imaging, as it can be aligned into a linear structure with a high aspect ratio. Second, it is stable. Third, it is readily available. As reviewed in the previous subsection, DNA origami has structures and nucleotide densities that are different than those of λ-DNA. These differences have not been studied in the literature, but are likely to impact the seeding and electroless plating of DNA origami. Other differences that may impact metallization include the small size of the
DNA origami, the stability of the origami, and the influence of the staple strands, typically found in excess in origami solutions [7].

2.4 Fabrication of DNA-templated Semiconductor Nanowires

Additional materials and deposition methods are needed in order to create useful devices structures on DNA templates. One method that has been used since 1996 [82] for the deposition of semiconductor materials onto DNA is to immerse DNA into a metal ion solution for hours or days, and then react the metal ions on DNA with a chalcogenide source (e.g. H\textsubscript{2}S, S\textsuperscript{2-}, Se\textsuperscript{2-}) to produce semiconductor nanoparticles. In a work reported by Dong et al. [83], this process was repeated to form continuous nanowires in a few days. The continuity of nanowires and the background deposition are tradeoffs. Additional deposition required for greater continuity also resulted in significant background deposition that is likely to be problematic for actual devices. CdS [82-84], CuS [85], CdSe [86], and CdSe/ZnS [87] nanowires or nanochains have been prepared in this way. The diameter of semiconductor nanowires, which may have a significant impact [88] on their physical properties, was difficult to control for these DNA-templated semiconductor nanowires or nanochains. Other useful semiconductor materials such as tellurium (Te), germanium (Ge), bismuth telluride (Bi\textsubscript{2}Te\textsubscript{3}) haven’t been deposited on DNA templates to form nanowires. Thus, for DNA-templated semiconductor nanowire fabrication, there are still a few challenges that haven’t been addressed in the literature: (1) the semiconductor materials that have been deposited onto DNA templates were limited to the metal chalcogenide semiconductors mentioned above, (2) the diameter of DNA-templated semiconductor nanowires was difficult to control, (3) the process for making these nanowires was quite lengthy, and (4) the selectivity of the semiconductor deposition was not very good, with significant background deposition. One
method that could simultaneously address all of these challenges is galvanic displacement of metal nanowires.

Galvanic displacement has been used to make a variety of metal and semiconductor materials, including Au, Pt, Pd [89, 90], Ag [91], In [92], Te [93-95], and Bi₂Te₃ [96]. Te and Te₂Bi₃ are both semiconductor materials [93, 97]. Specifically, Te and Te₂Bi₃ nanostructures were fabricated through galvanic displacement reaction with nickel and cobalt, as shown by Myung et al. [94-96]. To have a galvanic displacement reaction take place, the reduction potential of the material to be replaced should be more negative than that of the material to be deposited.

2.5 Summary

To conclude, DNA is a desired template for nanofabrication due to its small diameter, functional groups, designable sequence, and complementary base pairing. The development of DNA origami demonstrates that DNA can be folded into arbitrary 2D patterns and many 3D structures, providing a route for making the complex templates needed for nanoelectronic circuits and other nanodevices.

Metallization of DNA origami is important for the fabrication of nanodevices. However, the metallization of DNA origami has not yet been demonstrated in the literature prior to this study. This may be due to special properties of DNA origami, such as its small size, relatively low stability (compared to readily used λ-DNA), and the presence of a large excess of staple strands in DNA origami solutions. The ability to perform continuous, conductive, site-specific metallization of DNA origami has the potential to make a transformative impact on the development of nanodevices via self-assembled DNA templates.
Finally, nanodevice development would benefit from the ability to use a wider variety of materials on DNA templates. A few different methods have been developed successfully for the metallization of DNA to form conductive nanowires of different compositions. However, conductive DNA-templated nanowires of Ni, a non-noble metal, have not yet been demonstrated. In addition, there is a significant opportunity for new and better methods of depositing a variety of semiconductor materials onto DNA templates.
3 METALLIZATION OF BRANCHED DNA ORIGAMI FOR NANOELECTRONIC CIRCUIT FABRICATION

Use of DNA as a transistor template was demonstrated by Keren et al. who used λ-DNA and carbon nanotubes to create a DNA templated transistor [66]. While their pioneering work demonstrates proof-of-concept, it is not scalable to the complex architectures needed for future generations of devices. DNA origami has been demonstrated as a robust and simple method for creating arbitrary 2-D shapes [7] and different 3-D structures [33], offering a route to make templates that provide the increased complexity needed for nanoelectronic circuits. Recently, Pound et al. demonstrated the use of scaffolds of designed lengths prepared by PCR amplification to make branched DNA origami with thin, wire-like structures well suited for circuit templates [35]. Placement and orientation of DNA origami on a lithographically patterned surface has also recently been demonstrated [11, 75, 98]. However, metallization of DNA origami had not been demonstrated prior to my work.

3.1 Challenges and Strategies

The metallization of DNA origami presents several challenges relative to other DNA templates such as λ-DNA. First, DNA origami tends to be less stable than double-stranded λ-DNA, as it is held together by many short staple strands and may unfold. The metallization of DNA usually requires several steps that involve different solutions, concentrations and/or
temperatures; therefore, the DNA template must be sufficiently robust to maintain its shape when subjected to the conditions required for metallization. Second, the small size of the DNA origami makes surface adhesion more difficult due, for example, to fewer attachment points, and requires a higher degree of selectivity to enable identification on the surface after metallization. The small size also requires a high seed density and increased plating precision in order to yield continuous metallization of the DNA origami while preserving its shape. Third, a large excess of staple strands present in the DNA origami assembly solution, while increasing stability, can also impact the selectivity of DNA-origami metallization. This chapter describes my efforts to understand and address these challenges.

The branched DNA origami used in the current study is shown in Figure 3-1. This branched DNA origami was prepared as previously reported in the literature using 95 different types of staple strands [35]. All DNA origami structures used in this research were prepared by my collaborator, Elisabeth Pound of Department of Chemistry and Biochemistry at BYU. DNA origami was folded with both a 10:1 and a 100:1 molar ratio of staple strands to scaffold strands in either TAE-Mg\(^{2+}\) buffer (pH=8.5, 40 mM Tris-Base, 20 mM acetic acid, 1 mM EDTA, 12.5 mM MgAc\(_2\)) or Hepes-Mg\(^{2+}\) buffer (pH=7.4, 25 mM Hepes, 12.5 mM MgAc\(_2\)). This branched DNA origami is designed as an asymmetric structure with two 120 nm long top branches and a 75 nm long stem (Figure 3-1A). The top branches and the stem are 3 helices (~8 nm) and 4 helices (~11 nm) wide, respectively. Due to some flexibility in the junction where three branches intersect, this branched origami resembles a “T” or “Y” when deposited on mica surfaces (Figure 3-1B). All AFM images in this chapter were taken in air with tapping mode AFM. The height of the non-treated DNA origami on mica surfaces is about 0.6-1.1 nm.
Figure 3-1 (A) Design of branched origami. (B) AFM of branched origami deposited on mica. Scale bar: 500 nm. Height scale: 4 nm. (C) Schematic figure of metallization of branched origami.

3.2 Results and Discussion

A primary objective of work described in this chapter was to metallize branched DNA origami with little or no background metallization on the surface. In the results that follow, seeding was performed by reacting silver ions with aldehyde groups on chemically modified DNA origami in solution using a procedure modified from that described in Refs. [69-71]. Briefly, DNA origami was crosslinked with amine-modified psoralen (psoralen can covalently bind to two DNA strands by reacting with pyrimidine bases on these strands [99]) and then purified by dialysis. The DNA origami was then functionalized by reacting with glutaraldehyde, followed by another dialysis step to remove excess glutaraldehyde. Afterwards, DNA origami was seeded in solution with silver. Electroless plating of gold was subsequently performed on the silver seeds (see Section 3.4 for details).
Retaining the structure of DNA origami during the metallization processes is of key importance for nanocircuit fabrication. There are several aspects of the seeding and plating processes that have the potential to impact the stability of the DNA origami. For the metallization method used in this chapter, two of the most important variables are the composition of the rinsing solution and the amount of excess staple strands present in the dialysis procedure.

Rinsing is a frequently used step in DNA metallization processes that has the potential to influence DNA shape and stability. Initial experiments to examine the stability of DNA origami showed that even a 5 second rinse in ultrapure water was sufficient to cause substantial unfolding of the origami on mica surfaces (Figure 3-2A). However, if the DNA origami was deposited and rinsed (~5 seconds) with MgAc$_2$ (4mM) (Figure 3-2B) or MgCl$_2$ (4mM) (Figure 3-2C), it remained folded. Therefore, the presence of magnesium ions increased stability, presumably by reducing the repulsive force between negatively charged scaffold DNA and staple strands.

Figure 3-2. (A) AFM image of branched DNA origami on mica rinsed for 5 seconds with water. (B) AFM image of branched DNA origami on mica rinsed for 5 seconds with 4 mM MgAc$_2$. (C) AFM image of branched DNA origami on mica rinsed for 5 seconds with 4 mM MgCl$_2$. Scale bars: 500 nm. Height scales: 4 nm.
The seeding and plating processes use solutions of several different compositions, changing the environment to which the DNA origami is exposed and impacting its stability. Perhaps the most aggressive of these steps is the overnight dialysis against a water solution that is used to remove excess glutaraldehyde before seeding the DNA with silver \( [66-72] \). Indeed, I have observed unfolding of the origami during dialysis under several different conditions (Figure 3-3A). Attempts were made to enhance stability by crosslinking the assembled origami, dialyzing against a buffer solution containing \( \text{Mg}^{2+} \) (as opposed to just water), adjusting the initial concentration of the origami, and adjusting the staple to scaffold strand ratio.

The DNA origami was crosslinked with an amine-modified psoralen to enhance stability (see Section 3.4 for details). Initial results seemed to indicate an increase in stability, although the extent of crosslinking was not characterized precisely. The crosslinking also provides additional functional groups (i.e. amine groups) with the potential to increase the seed density by providing sites \([100]\) for metallization. Unfortunately, crosslinking alone did not provide the stability needed for effective dialysis of a 2 nM DNA origami solution with a 10:1 staple to scaffold strand ratio (Figure 3-3B). However, because of the positive initial results and the fact that the crosslinking did not have a negative impact on my process, I continued to use psoralen crosslinking with our samples.

Based on the increased stability observed when rinsing with solutions containing magnesium ions (see above), the stability of the origami was examined for overnight dialysis against a buffer solution containing \( \text{Mg}^{2+} \). The results in Figure 3-3C show that the DNA was not stable and unfolded during dialysis. Therefore, the potential increase in stability due to dialysis in 1X Hepes-\( \text{Mg}^{2+} \) buffer was not adequate to stabilize the DNA for a 2nM origami solution with a 10:1 staple to scaffold strand ratio.
Next, the staple to scaffold ratio was increased to 100:1, while the concentration of origami was kept at 2nM. The hypothesis behind this attempt was that the DNA stability was adversely affected by transfer of staple strands through the membrane during dialysis. Crosslinked DNA was used in order to increase the probability of success, and overnight dialysis was performed against both water (Figure 3-3D) and 1X Hepes-Mg\(^{2+}\) buffer (Figure 3-3E). The results for both of these dialysis solutions show that the DNA origami retained its structure and remained stable during overnight dialysis when the ratio of staple strands to scaffold strands was increased by a factor of 10. However, this 100:1 molar ratio of staple strands to scaffold has an adverse effect on the selectivity of metallization as discussed in detail later.

An additional experiment was performed in which the ratio of staple to scaffold strands was kept at 10:1, but the concentration of the DNA origami was increased to 10nM. This more concentrated solution was then dialyzed overnight against a 1X Hepes-Mg\(^{2+}\) buffer. Following dialysis, the solution was diluted by a factor of 10 and then deposited on the surface. The results show that the DNA did not unfold during dialysis and that the background concentration of staple strands was greatly reduced (Figure 3-3F). It also follows that the stability of the origami does not scale linearly with the staple strand to scaffold strand ratio, but is influenced by the absolute concentration of staple strands in solution. Also note that the quantity of DNA origami on the surface imaged by AFM was not only related to the concentration of DNA origami in the solution, but also the time allowed for surface deposition and rinsing.

From these results, silver seeding in solution was done using crosslinked branched origami dialyzed against 1X Hepes-Mg\(^{2+}\) buffer with both a 100:1 and a 10:1 molar ratio of staple strands to scaffold. Figures 3-4(A) and (B) show branched DNA origami (2 nM origami with 200 nM staple strands) deposited on a mica surface after seeding with silver in solution.
Magnesium addition (MgAc\(_2\), 10 mM) to the seeded DNA origami solution was used to promote adhesion of the seeded origami to the mica surface, followed by a moderate rinse by dipping into water to remove the seeding solution from the mica surface prior to plating. This moderate rinse step did not decompose or unfold the seeded DNA origami. The extent of seeding is difficult to determine from these images. The primary indication of seeding was an increase in height to 1.5 nm to 2.0 nm. The origami structures largely retained their shape and the entire structures appeared to be seeded, although the seeding was not completely uniform as indicated by a variation in height along the structures. Seeding of the background area is also evident in the images. The background deposition is believed to be due to excess staple strands on the surface as no such deposition was observed in the absence of DNA (Figure 3-4C). The observation that no significant plating was observed for samples that did not go through the seeding process provides strong evidence for both the need for and success of the seeding process.

With an increased understanding of how steps in the seeding processes influence the stability of DNA origami, I will now examine the plating process. Two types of control experiments were performed as a basis for evaluating metallization. First, the entire seeding (including the crosslinking and glutaraldehyde reaction steps) and plating procedures were performed with solutions that did not contain DNA. The expectation was that no plating would occur without the DNA template. The results shown in Figure 3-5A indicate little or no plating on a mica surface when there was no DNA present. The second control experiment was to deposit unseeded DNA on the surface and then subject it to the gold plating solution. No plating was observed on the unseeded DNA as evidenced by lack of significant change in the height of the structures on the surface (Figure 3-5B&C), even after long plating times (20 minutes, Figure 3-5D). There was an increase of 0.7nm-1nm in the height and a decrease in the length of origami
Figure 3-3. (A-C): AFM images of 2nM branched DNA origami with a 10:1 molar ratio of staple strands to scaffold after (A) glutaraldehyde reaction and overnight dialysis in water; (B) crosslinking, glutaraldehyde reaction, and overnight dialysis in water; (C) crosslinking, glutaraldehyde reaction, and overnight dialysis in 1X Hepes-Mg^{2+} buffer. (D-E) AFM images of 2 nM branched DNA origami with a 100:1 molar ratio of staple strands to scaffold after crosslinking, glutaraldehyde reaction, and (D) overnight dialysis in water; (E) overnight dialysis in 1X Hepes-Mg^{2+} buffer. (F) 10 nM DNA origami with a 10:1 molar ratio staple strands to scaffold after crosslinking, glutaraldehyde reaction, and overnight dialysis in 1X Hepes-Mg^{2+} buffer. Origami in (D) and (F) was diluted 10 times before deposition on mica surfaces. Scale bars: 500 nm. Height scales: 4 nm.

branches after 10 minutes’ incubation in the electroless Au plating solution. However, both the height and length did not change for a longer incubation of 20 minutes, which means the increase of height on origami is not due to metallic particles. It could be attributed to a combination of complexed Au ions on origami and the shrinkage of origami. We further used NaBH_4 solution (0.19M of NaBH_4, 4mM of MgCl_2) to reduce the origami treated with Au plating solution. After the reduction (Figure 3-5E), the height of origami decreased while the length of branches increased to about the same values as before the treatment of Au plating solution. And there were
only 1 or 2 small particles on origami (Figure 3-5E). These experiments establish the necessity of having seeded DNA templates on the surface for significant plating to occur.

![Image](image_url)

**Figure 3-4.** (A) & (B) AFM images of Ag seeded branched DNA origami, 2 nM scaffold with 100-fold excess staple strands, (C) AFM image of seeding on a control without DNA. Height scales: 4 nm. Scale bar in (A) & (C): 500 nm. Scale bar in (B): 250 nm.

Initial attempts to plate the seeded origami failed to show any DNA origami (plated or not plated) on the surface during AFM examination. Investigation showed that the problem was actually adhesion of the origami to the surface in the plating solution. The adhesion problem was solved by adding MgCl$_2$ to the electroless Au plating solution to yield a final Mg$^{2+}$ concentration of 2 mM.

Figure 3-6A shows an AFM image of a branched DNA origami that was metallized with gold. The starting DNA origami concentration was 2 nM with 100-fold staple strands. It was seeded and then plated with Au for 3 minutes to yield an average final height of 32 nm. The metallization appears to be continuous and the selectivity was sufficient to permit distinction of the metallized origami from the background. A lower magnification AFM image provides a surface view with multiple metallized origami, as well as background deposition (Figure 3-6B). The background deposition was attributed to seeded staple strands and some origami artifacts.
(i.e., two branches of origami stacked together, or tangled origami) as observed previously above (see Figure 3-3E).

Figure 3-5 A) AFM image after 3 minutes of exposure to the Au plating solution on a control surface without DNA. Height scale: 10 nm. AFM images of non-seeded origami after (B) 5 minutes, (C) 10 minutes, (D) 20 minutes of immersion in the Au electroless plating bath. (E): AFM image of non-seeded origami after 20 minutes of Au plating and 2 minutes of reduction by NaBH₄ solution (0.19M NaBH₄, 4mM MgCl₂) on non-seeded origami. Height scales: 4 nm. Scale bars: 500 nm.

To get better selectivity, the more concentrated DNA origami described above (10 nM, 10:1 staple to scaffold strand ratio) was used for metallization. Also, a smaller volume of DNA origami solution (10 μL, instead of 25 μL) was used in the seeding process and the seeded sample was rinsed by dipping in water for 5 seconds, rather than 2 seconds, after the origami was deposited onto the surface. The longer rinse after seeding removed a substantial fraction of the
staple strands from the surface, as well as some of the seeded origami. After subsequent electroless Au plating for 5 minutes, origami was seen plated with good selectivity (Figure 3-6C). The average height of the 5 minute plated origami was about 60 nm, which is significantly taller than the sample plated for 3 minutes (32 nm).

Scanning electron microscopy was also used to examine the morphology and continuity of the metallized, branched DNA origami. SEM images were taken in low-vacuum mode to avoid charging problems on the insulating mica substrate. These images (e.g., Figures 3-6D and 3-6E) provide evidence of continuous metallization. An EDX spectrum (Figure 3-6F) collected from the plated sample in Figure 3-6D confirms the presence of Au metal on the origami.

Additional experiments were performed to verify the role of staple strands during metallization, since they appear to represent the primary source for the background (non-selective) deposition. Figure 3-7 shows the results after both seeding (A) and plating (B&C) where the only DNA present was the staple strands (i.e., no origami). Substantial metallization was observed, consistent with the non-selective “background” plating observed in the experiments containing the DNA origami (see Figure 3-6A&B). It is interesting to note that the number of metal sites after plating was actually less than that observed immediately after the seeding process. The decreased deposition at lower magnesium concentrations is attributed to the preferential removal of staple strands, which are much smaller than the origami and adhere less strongly to the surface. Therefore, a lower Mg$^{2+}$ concentration (2 mM, lower compared to 10 mM Mg$^{2+}$ for adhering seeded origami to the surface) in the plating solution led to better selectivity for DNA origami metallization, while keeping enough origami on the surface.
Figure 3-6. (A) & (B): AFM images of 2 nM branched origami with a 100:1 molar ratio of staple strands to scaffold after Ag seeding and 3 minutes of Au plating. (C) AFM image of 10 nM branched origami with a 10:1 molar ratio of staple strands to scaffold after Ag seeding and 5 minutes of Au plating. (D): SEM image of 2 nM branched origami with a 100:1 molar ratio of staple strands to scaffold after Ag seeding and 3 minutes of Au plating. (E) SEM image of 10 nM branched origami with a 10:1 molar ratio of staple strands to scaffold after Ag seeding and 5 minutes of Au plating. SEM images were taken in low-vacuum mode. (F): EDX of the plated origami in image (D). Scale bars in (A-C): 500 nm. Height scales in (A-B): 120 nm. Height scale in (C): 150 nm.

Figure 3-7. (A) Seeded staple strands (200 nM of each staple strand, equivalent to a 100:1 staple to scaffold strand ratio) on a mica surface. Height scale: 6 nm. (B & C) Seeded, then 3 minutes of Au plating on staple strands. (B) & (C) are from AFM images of the same place with different height scales. Height scale in (B): 80 nm. Height scale in (C): 6 nm. Scale bars: 500 nm.
Experiments were also performed to examine the stability in the plating solution of DNA origami relative to that of λ-DNA, which is the most frequently used scaffold for DNA metallization. More than 80% (n=32) of λ-DNA strands deposited on a mica surface were longer than 10 microns (Figure 3-8A). After incubation in the Au electroless plating solution (with 2 mM MgCl₂) for 5 minutes, 96% (n=56) of DNA strands found on the surface were shorter than 5 microns long (Figure 3-8B). Apparently, the plating solution was instrumental in cleaving the λ-DNA. In contrast, the DNA origami maintained its structural integrity in the Au electroless plating solution (with 2 mM MgCl₂) over the same period of time (Figure 3-5B). The structural integrity of the origami is likely due to the presence of multiple helices connected at multiple points through staple strands. Even though some parts of the origami backbone may be cleaved, the principal structure of origami is retained. It was also observed that λ-DNA was not cleaved either in the plating solution (with 2 mM MgCl₂) without reducing agent or in only the reducing agent (with 2 mM MgCl₂). We observed similar behavior for λ-DNA exposed to an electroless Ni plating solution (20 g/L Na₂SO₄, 6H₂O, 16 g/L Na₂C₄H₄O₄·6H₂O, 27 g/L NaH₂PO₂·H₂O, 5 mM MgSO₄, pH=5.0, T=65 °C). A possibility consistent with these observations is that the DNA cleavage was caused by a reaction product from the plating reaction. Cleavage of the DNA backbone in an aqueous solution containing complexed metal ions, O₂/H₂O₂, and a reducing agent has been reported in the literature, and was attributed to the presence of hydroxyl radicals formed in solution [101, 102].
3.3 Conclusions

To conclude, metallization of branched, open-structured DNA origami with good selectivity has been demonstrated. DNA origami has the potential to provide the increasingly complex templates needed for nanocircuit fabrication. However, these structures also present several challenges for metallization as identified and addressed in this study. In particular, challenges associated with the stability of the origami structures during seeding and plating are important. Also, the presence of excess staple strands in solution has a significant impact on selectivity. The successful metallization of branched DNA origami demonstrated here represents important progress towards the realization of DNA-templated nanocircuits. The flexibility of designs possible with DNA origami can also be combined with selective metallization to enable future technologies such as next-generation sensors [103].
3.4 Materials and Methods

3.4.1 Materials

Glutaraldehyde and 4’-aminomethyltrioxsalen hydrochloride were purchased from Sigma-Aldrich, Inc.; AgNO₃, NH₃H₂O, and the Hepes buffer were obtained from Mallinckrodt Baker, Inc.; MgCl₂ and MgAc₂ were acquired from EMD Chemical Inc. Slide-A-Lyzer Mini Dialysis units (3500 MWCO) were purchased from Thermo Scientific (Pierce, Rockford, IL). The λ-DNA used in the study was from Worthington Biochemical Corporation. Mica was purchased from S & J trading, Inc., Glen Oaks, NY 11004. Water used in this research was purified by a Barnstead EASYpure UV/UF system (Barnstead│Thermolyne Corporation) and had a resistivity of 18.3 MΩ-cm.

3.4.2 DNA Origami Crosslinking

Five milligrams of 4’-aminomethyltrioxsalen hydrochloride was dissolved in 2 mL ethanol, wrapped with aluminum foil and kept in a fridge until use. 100 μL of DNA origami solution (either 2 nM or 10 nM origami) was mixed with 10 μL 500 mM NaCl and 10 μL 4’-aminomethyltrioxsalen hydrochloride and then refrigerated for 15 minutes. Subsequently, the solution was put on ice in a plastic petri dish under UV light (λ =365 nm) for 30 minutes. To remove excess 4’-aminomethyltrioxsalen hydrochloride, NaCl, and EDTA, the solution was dialyzed against 1X Hepes buffer (25 mM Hepes, 4 mM magnesium acetate, pH=7.4) for 10 hours in a fridge using a 3.5k MWCO membrane. The crosslinked and dialyzed DNA origami was then stored in a freezer at -20°C until use.
3.4.3 DNA Origami Modification and Seeding

Fifty microliters of crosslinked DNA origami solution was diluted to 100 μL with water, followed by the addition of 16 μL of 2.5% glutaraldehyde to react with the DNA origami. The reaction was allowed to take place at room temperature for 30 minutes. Afterwards, the sample was transferred onto ice for 20 minutes. The excess glutaraldehyde was then removed by dialysis (at least 24 hours) using a 3.5k MWCO membrane against ultrapure water or 1X Hepes buffer (25 mM Hepes, 4 mM magnesium acetate, pH=7.4) in the fridge. Subsequently, 25 μL or 10 μL of reacted DNA origami solution was diluted to 50 μL with water and then mixed with 50 μL basic silver nitrate solution (0.1 M AgNO₃, 0.33M ammonia hydroxide) in order for seeding to occur. The seeding process was allowed to proceed for 30 minutes in the dark on ice. Then, MgAc₂ was added to increase the Mg²⁺ concentration of the DNA origami solution to 10 mM. Afterwards, 4 μL of seeded DNA solution was put on a freshly-cleaved mica surface. The adsorption of DNA origami onto the mica surface was allowed to take place for 2 minutes. Negatively charged DNA can attach to negatively charged mica surface in the presence of an appropriate concentration of Mg²⁺. Then, the sample was rinsed by dipping in water for 2 or 5 seconds. After that, the water left on the mica surface was absorbed from the edge by a paper towel, and any remaining moisture was allowed to evaporate.

3.4.4 Electroless Plating

The plating solution was made by mixing equal volumes of 4 mM MgCl₂ and a commercial Au plating solution (GoldEnhance EM, Catalog #:2113, Nanoprobes, Yaphank, NY). Electroless Au plating solution was put on the surface immediately after the seeding process once the sample became dry. The electroless plating was allowed to proceed for 1-5 minutes. For the control samples, longer plating times of 7 and 10 min. were also explored.
Afterwards, the sample was rinsed with 4mM MgCl₂ for 5 seconds, and then with water for 2-3 seconds, followed by drying using a stream of filtered air.

3.4.5 SEM Imaging

Plated origami samples on insulating mica surfaces were imaged in low-vacuum mode on a Philips XL30 ESEM FEG. EDX analysis was also performed on this ESEM by using spot scan.

3.4.6 AFM Imaging

The samples were imaged in air using tapping mode on a Digital Instruments Nanoscope IIIa MultiMode AFM (Veeco) with silicon AFM tips (Vistaprobės, 3 N/m, 60-80 kHz).
4 SITE-SPECIFIC METALLIZATION OF DNA ORIGAMI FOR NANO ELECTRONIC CIRCUIT FABRICATION

After successful metallization of the complete, open-structured DNA origami with good selectivity, I move forward to site-specific metallization of branched DNA origami. As discussed earlier, site-specific metallization of DNA origami is needed so that designated spaces on DNA template can be left for the active components (i.e. semiconductor carbon nanotubes, elemental and compound semiconductors) of nanoelectronic circuits.

To achieve site-specific metallization on DNA origami, original staple strands at select locations on T-shaped DNA origami were replaced with staple strands modified at the end by adding A\textsubscript{10} (poly-adenine strands 10 bases long). These modified staple strands with the dangling A\textsubscript{10} strands provide potential attachment sites for Au NPs and are called binding sites in this chapter. In addition, 5 nm gold nanoparticles (Au NPs) were coated with thiolated T\textsubscript{8} (poly-thymine strands 8 bases long) DNA, complementary to the A strands at the binding sites, with use of a method similar to that reported previously [104]. Then, after filtering to remove excess staple strands (staple strands not incorporated into the DNA origami), the solution containing the DNA origami was mixed with a solution containing the Au NPs in order to attach the Au NPs to the DNA origami by base pairing between A and T (Figure 4-1). Technical details can be found in Section 4.2.
Figure 4-1 Scheme for site-specific seeding of DNA origami with Au NPs. DNA origami is folded with regular and modified (red) staple strands, giving a branched “T” structure. Modified staple strands are designed based on desired regions for metallization. Then Au NPs coated with complementary DNA are added and attached to the DNA structure.

4.1 Results and Discussion

4.1.1 Metallization of T-shaped DNA Origami Along One or Two Ttop Branches

4.1.1.1 Seeding in Solution

The T-shaped DNA origami has two longer, top branches (each 120 nm long) and one shorter branch (75 nm). Experiments were first performed to attach Au NPs to one of the top branches in solution (see Section 4.2). The ratio of the number of Au NPs to the number of DNA origami was 10:1 for these experiments. There are 33 binding sites along one 120 nm-long branch of DNA origami. Considering the size of the Au NPs, the length of the modified staple strands, and the distribution of these modified staple strands (binding sites), each binding site could be occupied by one Au NP (see Figure 4-2A for illustration of one Au NP attaching to one binding site on a DNA origami). So, a maximum of 33 Au NPs could attach to binding sites on
the DNA origami. However, based on the size of the Au NPs, the length of the modified staple strands, and the distribution of binding sites, it is possible for one Au NP to attach to up to 5 binding sites (see Figure 4-2B), which will reduce the number of Au NPs attached to the DNA origami. Meanwhile, the interaction between Au NPs (repulsion) will likely impact the deposition of Au NPs and reduce the actual number of Au NPs attached. Moreover, if some binding sites are not occupied, the number of Au NPs attached to DNA will be further reduced.

![Diagram](image_url)

**Figure 4-2: Illustration of the attachment of each Au NP to one (A) and five (B) binding sites on area of DNA origami with binding sites.**

The solution containing both DNA origami and Au NPs was diluted (to 0.33 nM of origami and 0.97 nM of Au NPs) and allowed to adsorb onto a mica surface for 90 sec. Figure 4-3A shows an AFM image of DNA origami seeded with Au NPs and then deposited on the mica surface. The T-shaped DNA origami was seeded successfully along one 120 nm-branch with
binding sites. However, a significant amount of background deposition due to Au NPs not attached to the DNA was also observed (Figure 4-3A). In an attempt to reduce the background deposition, the absorption time was decreased from 90 seconds to only 30 sec before rinsing. The results (Figure 4-2B) show that the background deposition caused by Au NPs was reduced significantly. Comparing Figure 4-3B to Figure 4-3A, the increase of deposition time from 30 sec to 90 sec resulted in about the same number of deposited DNA origami (~1.3 DNA origami per area of 1μm² in both deposition conditions; ~8 DNA origami per area of 1μm² if all DNA origami in the solution deposited onto the surface) on the surface but significant increase of Au NPs on the background. This could be because the smaller Au NPs move faster than the much larger DNA origami so that most of the mica surface was occupied by the Au NPs quickly, preventing further deposition of seeded DNA origami. Another possible way of reducing the background deposition is to remove excess Au NPs by filtering the DNA origami solution (after seeding) through a membrane. Based on my experience with the removal of unattached, thiolated T₈ by filtration from a solution containing these oligomers and Au NPs, I knew that Au NPs would not pass through a 30K MWCO membrane. These Au NPs will pass through a membrane with larger pores (100K MWCO). However, my attempts to use the larger membrane to remove the excess Au NPs from solution resulted in the undesirable removal of a large fraction of the seeded DNA origami. Consequently, filtration was not used to remove excess particles in the experiments reported here.

It was not possible to determine the exact number of seeds on the seeded DNA origami by AFM due to resolution limits of the instrument associated with the size of the tip. It was, however, possible to use the AFM to determine the sections of the DNA that were seeded and thus verify my ability to perform site specific seeding of the origami. The seeded DNA origami
on mica cannot be seen on SEM because of the low resolution for imaging the insulating mica surface under low vacuum mode. High resolution SEM and TEM imaging will be used in Section 4.1.1.3 to investigate the number of Au seeds and the gap between adjacent seeds on more important DNA origami seeded on a SiO$_2$ surface (since electrons of SEM can penetrate the 500 nm thick SiO$_2$ and be conducted away, high resolution SEM can be used for imaging these samples under high vacuum mode without the charging problem created by the substrate).

![AFM images](image)

**Figure 4-3**: AFM images of one-branch seeded, T-shaped DNA origami deposited on a mica surface for 90 sec (A) or 30 sec (B). Scale bars are 500 nm. Height scales are 10 nm.

After attaching Au NPs successfully to one branch of the DNA origami, a “T” shaped origami with staple strands modified to attach Au NPs along both of the top branches was folded. Initial experiments for seeding both of the top branches of the T-shaped DNA origami in solution showed that DNA origami failed to retain its shape after seeding (Figure 4-4A&B). The unseeded branch can still be seen clearly in a high-magnification AFM image (Figure 4-4B). However, the length of the top branches of the T-shaped DNA origami after seeding was only about 136 nm (measured on AFM, Figure 4-4B), a value very close to that of one seeded branch.
The height of the seeded part is about 5.5-7.5 nm (Figure 4-4C). Based on these observations, it’s believed that gold particles were able to bind simultaneously to sites on both of the two branches (of the same DNA origami), causing the two branches to fold onto each other to form one seeded segment. Since the T-shaped DNA origami is flexible at the branch point (the point where three branches intersect) and relatively stiff in the axial direction, one branch with unfilled binding sites could move around the branch point (axial pivot point) and attach to the available Au NPs at the symmetric location on the other branch. This presents a challenge for seeding both top branches of T-shaped DNA origami. This challenge may be addressed in multiple ways, for instance through the use of staple strands with different binding sequences on each branch. In this study, I resolved the matter by adsorbing DNA origami onto a surface prior to seeding so that the movement of the branches was restricted. The Au NPs were then added and allowed to interact with the DNA origami on the surface.

4.1.1.2 Seeding on a Mica Surface

To solve the problems of seeding DNA origami in solution, mica, a common substrate for DNA deposition, was selected as the surface for the adsorption of DNA origami prior to seeding. Mg$^{2+}$ is used to facilitate the attachment of negatively charged DNA to a negatively charged mica surface. On the T-shaped origami used in this research, there were 67 binding sites along the top branches (see Figure 4-1 for the distribution of the binding sites). Considering the size of Au NPs, the length of the modified staple strands, and the distribution of these modified staple strands, each binding site could be occupied by one Au NP. According to the analysis presented earlier in this chapter (see Section 4.1.1.1), a maximum of 67 Au NPs could be attached to these binding sites along the top branches of the DNA origami, however, the actual number of Au NPs attached could be significantly less than this value.
Experiments were performed by depositing T-shaped DNA origami (top branches with binding sites) on a mica surface and then seeding the origami by exposing it to a solution containing Au NPs (coated with thiolated T₈ DNA) for 15 min to 1 hr at room temperature in a humid chamber in order to prevent evaporation (see Section 4.2). The influence of the concentration of Au NPs and the seeding time on the observed extent of seeding was investigated. As mentioned in Section 4.1.1.1, the seeded DNA origami on the mica substrate cannot be seen on SEM. Thus, AFM was used for initial imaging of the seeded DNA origami.
Figure 4-5A-C shows AFM images of DNA origami seeded with 12 μL of 1.2 nM Au NPs on a mica surface for 15 min, 30 min, and 1 hr, respectively. The average density of DNA origami structures presented on these samples was about 0.27 per 1 µm². The number of Au NPs ($8.5 \times 10^9$) in the seeding solution was estimated as 265 times the number of DNA origami ($3.2 \times 10^7$) on the mica surface (the placement of liquid volume on the surface was accurate using a micropipette and was very reproducible). Figures 4-A-C show that the seeded DNA origami appeared continuous at places. However, the actual seeding is not likely to be continuous, and the appearance of continuity is due to the tip-induced widening [47].

While resolution limits prevent determination of the precise number of Au NPs on the DNA origami, the AFM images clearly show that DNA origami was seeded, and that the seeding was not completely uniform as evidenced by the presence of gaps between seeded areas on some DNA origami (see Figure 4-5D, a zoom-in image of Figure 4-5C). Data collected from AFM images show that the ratio of seeded DNA origami with one or more visible gaps to all of DNA origami on the imaged area on the mica surface is 14/21 (0.67), 12/17 (0.71), and 12/18 (0.67) for samples seeded for 15 min, 30 min, and 1hr, respectively. So, increasing the seeding time from 15 min to 1 hr did not reduce the probability of finding gaps on the seeded DNA origami. Figures 4-5A-D also show that the background deposition was low for all of the seeded samples, independent of the seeding time. Additionally, I know that DNA origami can be seeded in 15 min from this experiment.
Figure 4-5: Seeding on a mica surface at room temperature in a humid chamber with different seeding times or seed concentrations. A-C: AFM images of T-shaped origami (with binding sites along top branches) seeded for 15 min (A), 30 min (B), and 1 hr (C&D) with 12 μL of 1.2 nM Au NPs (with thiolated T₈ DNA). (E) AFM image of T-shaped origami (with binding sites along top branches) seeded for 15 min with 12 μL of 6 nM Au NPs (with thiolated T₈ DNA). Height scales: 10 nm. Scale bar is 500 nm in (A,B,C, and E) and 200 nm in (D).

In the next step, I investigated the seeding of DNA origami on surface for 15 min with a higher concentration of Au NPs. Figure 4-5E shows the results for DNA origami seeded with 12 μL of 6 nM Au NPs (results quite reproducible, almost the same results on 9 samples). The average density of DNA origami structures presented on these samples was about 0.26 per 1 μm². Counting the exact number of seeds on these samples with AFM is not feasible. However, data collected from AFM images show that the ratio of seeded DNA origami with one or more visible gaps to all of DNA origami on the imaged area on mica surface is 1/27 (0.04), significantly smaller than that from samples seeded with a lower concentration of Au NPs. Thus, it is reasonable to conclude that a higher concentration of Au NPs can lead to a higher seeding
density on DNA origami, likely due to the higher chances of collisions between Au NPs and binding sites on DNA origami. With this higher concentration of Au NPs for seeding, the background deposition also became more significant. Therefore, the concentration of Au NPs can impact the density and selectivity of DNA origami seeding on a mica surface. The temperature might also have an impact on the seeding results, but was not investigated in this study since room temperature yielded good and reproducible results.

4.1.1.3  Seeding on a SiO$_2$ Surface

In the semiconductor industry, electronic devices are fabricated through photolithography performed on the silicon wafer. Thus, after the successful seeding of the top branches of T-shaped DNA origami on mica surfaces, we also seeded this DNA origami on a silicon wafer with 500 nm silicon oxide on the surface (oxide was thermally grown) for the possible integration with the conventional photolithography. A method reported by Kershner et al. in 2009 [11] was adopted here to deposit DNA origami onto a SiO$_2$ surface. First, the surface was plasma cleaned (18W of power applied to RF coil, 8-12 MHz) for 30 sec to remove contaminants. The surface became hydrophilic after plasma cleaning due to exposed silanol groups. Before surface deposition of DNA origami, a filtering process was performed to remove excess staple strands (67 out of 95 types of staple strands used to assemble T-shaped origami were modified staple strands which could impact the seeding if deposited onto the SiO$_2$ surface). Experiments showed that at least 90% of staple strands were removed in the filtering process (see Section 4.2 for details). Then, 3 μL of 2 nM, filtered DNA origami (~ $3.6 \times 10^9$ DNA origami structures) in 10X TAE buffer (125 mM MgAc$_2$, 400 mM Tris Base, 200 mM acetic acid and 10 mM EDTA, pH=8.3) was deposited by dropping the solution onto the hydrophilic surface and allowing it to
spread. The plasma cleaned SiO$_2$ surface was exposed to the solution for 2 hrs in a humid chamber (see Section 4.2 for details) in order to permit adsorption of the DNA to the surface. Consistent with reference [11], a Mg$^{2+}$ concentration of ~100 mM was used to bind negatively charged DNA structures to the plasma cleaned, negatively charged SiO$_2$ surface.

When 3 μL of 2 nM, filtered DNA origami was directly deposited on the SiO$_2$ surface for 2 hrs, the density of DNA origami deposited on the SiO$_2$ surface was about 12.5 per 1 μm$^2$ (Figure 4-6A). The droplet covered almost the whole surface of the wafer (found in 102 samples out of all 104 samples). Thus, the total number of DNA origami deposited on the whole SiO$_2$ surface of was ~1.25×10$^9$ (35% of the DNA origami in solution). A relatively large fraction of the DNA origami overlapped on the surface (Figure 4-6A, marked by red triangles). The total number of DNA origami deposited on the SiO$_2$ surface was more than that on the mica surface, so that a higher concentration of Au NPs was needed here for seeding. I anticipated that with a higher concentration of Au NPs than that used on mica, the chances for Au NPs and binding sites to collide were higher so that the ratio of Au NPs/DNA might not need to be as high as that on mica (for instance, may be smaller than 265). Thus, after the deposition of DNA origami on a SiO$_2$ surface, 12 μL of 12 nM Au NPs (8.7×10$^{10}$ Au NPs, a ratio of 70 times Au NPs per DNA origami on the SiO$_2$ surface) in 10X TAE buffer was deposited onto the surface and allowed to interact with the DNA origami for 30 min in a humid container. DNA origami, even overlapped, was seeded successfully on the SiO$_2$ surface and the seeding appeared continuous in the AFM image (Figure 4-6B, overlapped origami structures were marked with red triangles). The background deposition was lower than that on mica using a lower concentration of Au NPs (Figure 4-5E), which could be due to the differences between the SiO$_2$ surface and the mica surface. Depending on how the DNA origami was deposited onto the SiO$_2$ surface, the average
total length of the seeded portion measured on the AFM was 197 nm, \( s = 39 \text{ nm}, 14 \text{ DNA origami counted} \), which was significantly shorter than that of isolated DNA origami on the SiO\(_2\) surface before seeding (244 nm, \( s = 7.6 \text{ nm}, 14 \text{ DNA origami counted} \)). The problem was resolved by using a lower concentration (0.67 nM) of DNA origami solution in the surface deposition process as described below, in which less DNA origami was deposited on the surface, and a large fraction of the deposited origami was isolated to yield a measured average length of 250 nm. This indicates that the interaction between DNA origami on the surface contributed to the shorter measured length of the DNA origami after seeding.

![Figure 4-6: 2 nM of filtered, T-shaped, top branches modified DNA origami deposited on a SiO\(_2\) surface for 2 hours (A) and seeded on the surface with thiolated T\(_8\) DNA coated Au seeds (B). Triangles mark overlapping DNA origami. Scale bars are 500 nm. Height scales are 6 nm.](image)

To understand the cause of DNA overlapping, DNA origami was deposited onto a SiO\(_2\) surface for a range of deposition times. The results are shown in Table 4-1. For instance, when DNA origami was deposited onto a SiO\(_2\) surface for 1 min (Figure 4-7A), 171 DNA origami structures were present in an area of 10 \( \mu \text{m} \) by 10 \( \mu \text{m} \), with 14 of DNA origami structures overlapping one another (8% of the total). It was observed that both the total number of DNA origami and percentage of overlapping DNA origami increased (Table 4-1) when the deposition
time was increased to 3 min (Figure 4-7B), 5 min (Figure 4-7C), and 10 min (Figure 4-7D). This reveals that the gradual deposition of DNA origami on one another, likely due to the limited surface area, contributes to overlapping of the deposited DNA origami on the SiO$_2$ surface. For long deposition times, the majority of the DNA overlap was due to deposition from solution onto DNA already on the surface rather than the interaction of DNA in solution.

Figure 4-7: AFM images of DNA origami deposited on a SiO$_2$ surface for 1 min (A), 3 min (B), 5 min (C), and 10 min (D). Scale bars are 500 nm. Height scales are 6 nm.
Table 4-1: Deposition of 2 nM, filtered DNA origami onto a SiO₂ surface at room temperature for 1 min, 3 min, 5 min, and 10 min, respectively.

<table>
<thead>
<tr>
<th>Deposition time (min)</th>
<th>Total number of DNA origami in 10µm x 10µm image</th>
<th>Overlapping DNA origami in the image</th>
<th>Ratio of overlapping DNA origami to total DNA origami</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>171</td>
<td>14</td>
<td>8%</td>
</tr>
<tr>
<td>3</td>
<td>345</td>
<td>56</td>
<td>16%</td>
</tr>
<tr>
<td>5</td>
<td>378</td>
<td>98</td>
<td>26%</td>
</tr>
<tr>
<td>10</td>
<td>570</td>
<td>197</td>
<td>35%</td>
</tr>
</tbody>
</table>

To reduce the amount of overlapping DNA origami on the surface and also to use as little DNA origami as possible, we used a diluted DNA origami solution (0.67 nM) for the surface deposition (2 hrs). An AFM image of the surface after deposition of the origami (Figure 4-8A) shows that most of the DNA origami were isolated and retained their structure on the SiO₂ surface. The average length of the top branches (containing the binding sites) was about 250 nm ($s = 6.1$ nm, 14 DNA origami counted). At the lower concentration, the total amount of DNA origami in the solution was lowered so that the chance of overlapping on the surface was reduced. After seeding on a SiO₂ surface for 30 min (Figure 4-8B&C), the majority of the DNA origami was still isolated and was well seeded (Figure 4-8B&C). The average length of the seeded portion of single DNA origami structures was 249 nm ($s = 18$ nm, 16 DNA origami counted), close to the length observed before seeding, and significantly longer than that observed for seeded origami that were deposited from a more concentrated 2 nM solution (Figure 4-8C). This desirable structure and length of seeded DNA origami was likely due to the use of diluted DNA origami (0.67 nM), which deposited on the surface in an isolated fashion with good structure.

The seeding of DNA origami on SiO₂ looks continuous on the AFM (Figure 4-8B, started with 0.67 nM of DNA origami for surface deposition; seeded with 12 µL of 12 nM Au NPs on
the surface). However, as mentioned earlier, the AFM is not accurate in measuring the width and length due to the radius of the AFM tip. Therefore, high resolution SEM images were taken.

SEM images such as that in Figure 4-8D shows that on average there were 16 Au NPs \((n = 10, s = 3.3)\) on the seeded portion of the DNA origami. All the spacing mentioned in this chapter means the closest distance from one Au NP to another Au NP. For example, when two 7.6-nm Au NPs are touching each other, the spacing between these two Au NPs is 0 nm. Although the largest spacing between adjacent seeds on one seeded DNA origami structure is at least 12 nm, the average and median spacing between adjacent seeds is 5.8 nm and 4.1 nm, respectively. The TEM image (Figure 4-8E) shows more clearly the distribution of Au NPs on the seeded DNA origami.

Based on these observations, it is likely that 3 binding sites attached to one Au NP at the majority of sites on top branches of the T-shaped DNA origami (Figure 4-8F), and at some locations one or two binding sites attached to one Au NP. Meanwhile, some binding sites (where the 12 nm or larger spacings were located) did not bind to any Au NPs. From the experiments and analysis above, it’s obvious that the density and the distribution of binding sites are very important for the small spacing accomplished here, while the size of Au NPs and the length of binding strands also have impacts. The existence of one or two large spacings \((\geq 12 \text{ nm})\) on most seeded DNA origami could be due to the insufficient opportunities for the binds sites to collide with and bind to the Au NPs. These large spacings could be reduced by filling with Au NPs if a higher concentration of Au NPs or a significantly longer time (i.e. 24 hrs, instead of 30 min) is used for the seeding.
Figure 4-8: 0.67 nM of T-shaped, top branches-modified DNA origami deposited on a SiO$_2$ surface (A) and seeded (B-E) with 12 μL of 1.2×10$^8$ M Au NPs (coated with thiolated T$_8$ DNA) on the surface. (A-C): AFM images. (D): SEM image. (E) TEM image. (F): Deduced attachment of Au NPs (coated with thiolated T$_8$ DNA) to binding sites on T-shaped DNA origami (along the top branches) based on my experimental data. Height scale is 6 nm in (A & B) and 20 nm in (C). Scale bar is 500 nm in (A-C), 200 nm in (D), and 50 nm in (E).
Despite the existence of a spacing between adjacent Au NPs on DNA origami in the work here, this spacing is significantly smaller than that reported recently by Pais et al., where the typical spacing was ~15 nm (center to center distance between 5-nm Au NPs was 20 nm) [77]. Compared to the work of Pais et al., I have a significantly higher [thiolated DNA strand]/[Au NP] ratio (200:1, compared to 5:1 by Pais et al.) in the mixture for the attachment of Au NPs to DNA origami. In the literature, it was believed that Au NPs were fully covered by oligomers when this procedure for attaching oligonucleotides to Au NPs was used [104]. Demers et al. [105] showed that the surface coverage of 12-base, thiolated DNA strands on 16 nm- Au NPs was as high as 34 pmol/cm². Au NPs of a smaller size produce a higher surface coverage by thiolated DNA strands [106]. Even if the surface coverage of 34 pmol/cm² is applied to my system, the number of thiolated DNA strands attached to each 7.6 nm-Au NP would be 37, significantly higher than 5. Thus, it’s believed that the number of thiolated DNA on each Au NP is much higher in my system than that in the work by Pais et al. This significantly higher number of thiolated DNA strands (attachment points) could lead to the increased opportunity of attaching Au NP to the binding sites on DNA origami in my work. Additionally, shorter sticky strands (8 bases or 2.7 nm on this work, compared to 29 bases, or 9.9 nm in reference [77]) was used here on the DNA origami for the attachment of Au NPs, so that the attached Au NPs could have less chance of attaching to the neighboring binding sites. Thus, there is a higher chance in my system that the unfilled binding sites near the filled ones on DNA origami can bind Au NPs in solution and increase the number of Au NPs attached to DNA origami. The attachment of Au NPs to DNA could be used for the site-specific metallization of DNA origami templates for nanoelectronic applications. The higher density of seeding (smaller spacing between adjacent Au NPs on DNA origami, compared to that in [77]) achieved here will require less plating to
connect adjacent Au NPs and lead to continuous nanowires of a smaller diameter after electroless plating.

4.1.1.4 Plating on DNA Origami

Plating on a Mica Surface

Electroless Au plating was performed in this study to form continuous nanowires from the discrete seeds deposited on specific areas of the DNA origami. The use of electroless Ag plating to connect Au NPs on DNA origami and form a variety of shapes was reported recently by Pais et al. in a work parallel with that presented here [77]. Here, I chose Au plating because Au nanomaterials could have a variety of uses, including electronic, optical, and biomedical applications [107, 108]. For instance, due to the chemical inertness, simple bioconjugation, and good biocompatibility of Au, Au nanorods could be used for photothermal treatment and optical imaging in biomedical research [108]. Consistent with the work presented in the previous chapter, 2 mM of MgCl₂ was added to the electroless Au plating solution in order to help keep DNA origami on the surface.

Initial plating performed on one-branch seeded, T-shaped DNA origami (seeded in solution) deposited on mica showed that the DNA origami was unfolded after immersion in the plating solution (Figure 4-9). As concluded in Chapter 3, non-seeded DNA origami was still in a good shape after immersion in this Au plating solution with 2 mM of MgCl₂. It’s possible that the negatively charged Au NPs added onto DNA increased the electrostatic repulsion between the negatively charged DNA origami scaffold and negatively charged staple strands with Au NPs and requires a higher concentration of Mg²⁺ to neutralize this effect. In the seeding step, DNA origami was seeded with Au NPs in TAE buffer with 12.5 mM MgAc₂ and retained the structure.
after seeding. Thus, Au NPs attached DNA origami is stable in the seeding solution with 12.5 mM MgAc$_2$. Consequently, to maintain the structure of seeded DNA origami during the plating on a mica surface, a concentration of 10 mM (close to 12.5 mM, much higher than 2 mM) of MgCl$_2$ was added into the Au plating solution.

As a result, DNA origami maintained the shape after plating. Figure 4-10 displays AFM images of T-shaped DNA origami (one branch seeded) on mica, plated for 30 sec, 1 min, and 2 min. The average height of plated DNA origami in Figures 4-10A, B, and C was 13 nm, 22 nm, and 42 nm, respectively. Au plating of 2 min on seeded DNA origami led to nanowires with an average width of 41 nm ($s = 10.5$ nm, 21 nanowires measured), as shown by SEM images (Figure 4-11). The smallest, continuous nanowires obtained after 2 min of Au plating on mica were about 25 nm in width (Figure 4-11B).
Figure 4-10: AFM images of one branch seeded DNA origami plated using an electroless Au plating solution with 10 mM Mg\textsuperscript{2+} for 30 sec (A), 1 min (B), and 2 min (C) on a mica surface. (D-E) are same AFM images as (A-C) with different height scales. Height scale is 4 nm in (A-C), 30 nm in (D), 45 nm in (E), and 60 nm in (F).

Figure 4-11: SEM images of one-branch seeded T-shaped DNA origami plated on mica using an electroless Au plating solution with 10 mM of Mg\textsuperscript{2+}. Scale bar is 1 micron in (A) and 100 nm in (B).
Plating on a SiO\textsubscript{2} Surface

The same Au plating solution with 10 mM of MgCl\textsubscript{2} that was used successfully to plate DNA origami on a mica surface was next used to plate T-shaped DNA origami on a SiO\textsubscript{2} surface. At first, Au plating was performed on the SiO\textsubscript{2} surface with diluted DNA origami (0.67 nM) deposited on the surface. SEM imaging (i.e. Figure 4-12) shows that while some origami appear continuous after 2 min of Au plating, the majority of DNA origami structures were still not continuous. Moreover, the density of DNA origami on the surface after plating was not high enough to enable the conductivity tests because DNA origami were not oriented and the electrode pads (with gaps of 160 nm) would be randomly deposited onto the surface.

Thus, I investigated the plating on the DNA origami with a higher concentration of origami (2 nM) when deposited onto the SiO\textsubscript{2} surface. Figure 4-13 shows SEM results for samples plated for 1, 2, 5, and 20 min, respectively. As a result, significantly more origami structures were found on the surface after the plating. After 1 min of plating, the average height of seeded DNA origami increased from 7.0 nm (s = 1.1 nm, 63 sites counted) to 13.6 nm (s = 3.2 nm, 60 sites counted) with the unseeded branch still recognizable on the AFM image (Figure 4-
The height was measured by AFM. SEM imaging (Figure 4-13A&B) shows that the plating was not continuous. The unseeded branch can’t be seen in the SEM. The average width of plated origami was 13.0 nm ($s = 3.0$ nm, 34 sites counted). The width was obtained from SEM images by measuring multiple points on different DNA origami. At places where there were gaps between adjacent particles, only the widths of particles were measured. When plated for 2, 5, 10, and 20 min, the respective height and width can be seen in Table 4-2. It was not surprising that the measured width of samples plated for 5 min was smaller than that plated for 2 min because many gaps were filled with small wires during 2 min to 5 min. The plating rate decreased substantially with time indicating the potential importance of transport. This is supported by the results of a simple calculation assuming semi-infinite diffusion (see Section 4.2.10 for the calculation) that indicates that the concentration of reactants in the solution near the surface becomes significantly depleted after 1 minute of plating for our experimental conditions. This decrease would slow down the plating reaction and lead to non-uniform plating at places with different local concentrations of reactants.

It is also possible that this modified, commercial plating solution contains additives that accelerate the plating. If the additives are consumed in the plating, the plating rate may be limited by the diffusion of additives to the Au surface, rather than the diffusion of gold ions.

Another possible explanation for the decrease of the plating rate with time is that the surface density of additives (which accelerate the plating) decreases as the particle size increases. In this case, the seeds would grow to a more uniform size as the plating goes on. This endpoint, however, is in conflict with the observation that the standard deviation of the width and height of wires both increased with time (see Table 4-2).
Figure 4-13: SEM images of Au NP seeded and Au plated DNA origami. A&B) Origami electrolessly plated with Au for 1 minute. C&D) Origami plated for 2 minutes. E&F) Origami plated for 5 minutes. G&H) Origami plated for 20 minutes. Scale bar is 200 nm in all images.
Figure 4-14: AFM image of T-shaped DNA origami (2 nM) seeded along top branches and plated for 1 min with a modified commercial Au plating solution. Scale bar is 200 nm. Height scale is 6 nm.

Table 4-2: Height and width of T-shaped DNA origami (2 nM) seeded along top branches and plated for a range of plating times. “s” denotes standard deviation and “n” denotes the number of sites measured. Height was measured by AFM. Width was measured from SEM images.

<table>
<thead>
<tr>
<th>Plating Time on T-shaped origami seeded along top branches (min)</th>
<th>Height (nm)</th>
<th>Width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.0 (s = 1.1, n = 63)</td>
<td>Not available</td>
</tr>
<tr>
<td>1</td>
<td>13.6 (s = 3.2, n = 60)</td>
<td>13.0 (s = 3.0, n = 102)</td>
</tr>
<tr>
<td>2</td>
<td>17.8 (s = 4.1, n = 29)</td>
<td>19.8 (s = 4.3, n = 132)</td>
</tr>
<tr>
<td>5</td>
<td>20.4 (s = 4.5, n = 29)</td>
<td>18.3 (s = 6.1, n = 204)</td>
</tr>
<tr>
<td>10</td>
<td>28.1 (s = 6.5, n = 34)</td>
<td>19.8 (s = 7.2, n = 156)</td>
</tr>
<tr>
<td>20</td>
<td>29.0 (s = 7.5, n = 33)</td>
<td>25.0 (s = 11.4, n = 177)</td>
</tr>
</tbody>
</table>

When plated for 2 min (plated origami was 19.8 nm wide, an increase of about 12.2 nm from the Au seeds), metallization appeared continuous for some DNA origami (Figure 4-13C&D), although the majority of DNA origami structures were still not continuous. This is
consistent with the seeding results on DNA origami structures, where the maximum spacing
between adjacent Au seeds on each origami structure ranges from 12 nm to 36 nm with an
average value of 20 nm. To fill a 12 nm spacing, the diameter of neighboring two seeds needs to
increase by at least 12 nm (assuming a hemispherical growth model for these two seeds),
resulting continuous nanowires 20 nm or greater in width.

The rate of increase of the height of plated DNA origami (plating rate) decreased with
time, as shown in Figure 4-15. No significant height difference was observed when comparing
the samples plated for 10 min and 20 min (Figure 4-15). This is consistent with plating that is
mass transport controlled, rather than kinetically controlled [109, 110]. Figures 4-13G&H show
SEM images of seeded DNA origami after 20 min of plating. Although some continuous
nanowires were present on the surface, many of the nanowires were still not continuous and the
seeds appeared to grow at different rates on the DNA origami. The Au NPs attached to DNA
origami before electroless plating were not perfectly uniform and had an average diameter of 7.6
nm with the standard deviation of 0.8 nm, as studied with TEM. Non-uniform plating would be
expected under mass transport limited conditions, during which the plating takes place
preferentially on sites with easier access to the reactants (for example, larger seeds).

To verify the assumption that the plating was mass transport limited, a control experiment
was performed where plating was done on sparse Au seeds (less than 15 Au seeds in an area of
10 μm by 10 μm) deposited on a SiO₂ surface (Figure 4-16A). In this experiment the seeds grew
to an average height of 49 nm in 2 min (Figure 4-16B), much taller than that on the seeded DNA
origami discussed above. The significantly higher plating rate on separate Au NPs in the control
experiment, relative to the rate observed for closely packed Au NPs on DNA origami, supports
the conclusion that the plating on Au NPs on DNA origami was mass transport limited. It could be limited by the diffusion of Au ions, the reducing agent, or additives. For the control experiment, the Au NPs were far away from one another and the concentration profile associated with each particle was not influenced appreciably by the presence of the other particles. In contrast, the Au NPs on DNA origami were very close to each other and origami structures were also densely deposited on the surface; therefore, Au NPs on DNA origami interacted and competed with each other for reactants during the plating process.

Figure 4-15: The correlation between the average height of plated DNA origami and the plating time.

The depletion of reactants during the plating of Au NP-seeded DNA origami implies that a higher plating rate could be achieved if multiple plating steps, each using a fresh plating solution, were done for single sample. Experiments where a seeded DNA origami surface was plated twice with fresh plating solution, each time for 3 min, resulted in plated DNA origami which had an average height of 32 nm, greater than that of the sample plated once for a much longer time of 20 min. SEM imaging (Figure 4-17A&B) shows a beads-on-a-string effect where larger plated particles on the DNA origami were connected by nanowires of much smaller
diameter. This may be explained by a mass transfer limited plating process. At the beginning of each plating process, the local concentrations of reactants are uniform on the surface and each Au NP can grow larger. Later, when the solution near the surface was significantly depleted due to the reaction, the smaller particles on the origami grew very slowly or no longer grew. When this plating process was repeated with a fresh plating solution, the smaller particles grew a little more again in the beginning of the plating and formed the “strings” between the well-plated, much larger “beads” observed by the SEM. The width of plated DNA origami ranged from 10 nm (string) to 62 nm (bead), with an average value of 35.0 nm and a standard deviation of 14.4 nm (123 sites counted). Based on the above, it seems clear that the plating of T-shaped DNA origami (2 nM) with the modified commercial Au plating solution was mass transport limited. It could be limited by the diffusion of Au ions, the reducing agent, or additives.

Figure 4-16: AFM images of Au NPs (with thiolated T₈ DNA) on the silicon dioxide surface before (A) and after (B) plating with the modified commercial plating solution for 2 min. Height scale is 8 nm in (A) and 100 nm in (B). Scale bars are 2.5 μm.

To obtain more uniform results, I used an electroless Au plating solution that achieved uniform plating on Au-seeded λ-DNA when used by Satti et al. [54]. The plating solution was
used earlier by Natan et al. [111] to enlarge Au NPs both in aqueous solutions and on 3-(mercaptoproplyl)trimethoxysilane modified glass substrates. This Au plating solution consists of HAuCl₄ and NH₂OH [111]. Control plating experiments showed that this plating solution did not plate on the Au NPs (coated with bis(p-sulfonatophenyl) phenylphosphine dihydrate dipotassium, oligonucleotides, and maybe also some citrate groups) attached on the DNA origami as no height or diameter change was observed on seeded DNA origami when immersed in the plating solution for 10 min. However, when the hydroxylamine Au plating solution was used to plate DNA origami that previously had been plated for 1 min to a width of 11.9 nm by the modified commercial Au plating solution, the width of plated DNA origami increased. SEM imaging (Figure 4-17C&D) showed the width of the plated origami ranging from 19.4 nm to 38.9 nm with an average value of 33.0 nm (s = 7.3 nm, n = 133). This standard deviation is only about half of that for DNA origami plated to a similar width with the modified commercial Au plating solution. Thus, the use of the hydroxylamine Au plating solution increased the uniformity of nanowires over those formed with the modified commercial Au plating solution.

Conductivity tests were performed in a parallel study at BYU on these T-shaped origami structures metallized along the top branches. The samples used for conductivity tests were plated with the modified commercial Au plating solution for 1 min, and then the hydroxylamine Au plating solution for 2 min. The electrodes needed for the conductivity tests were patterned on top of the SiO₂ surface with plated origami using electron-beam lithography. The conductivity tests showed that the Au plated origami was conductive with an average resistivity of 5×10⁻⁶ Ω-m, which was more than 2 orders of magnitude higher than that for bulk gold (2.44×10⁻⁸ Ω-m), similar to the difference between the bulk conductivity and nanowire conductivity observed by others [36, 37, 54, 56, 67, 70, 71, 81].
Figure 4-17: A & B are SEM images of T-shaped DNA origami (2 nM) seeded along top branches and plated twice for 3 min with a modified commercial Au plating solution. C & D are SEM image of T-shaped DNA origami (2 nM) seeded along top branches and plated with a modified commercial Au plating solution for 1 min and the hydroxylamine Au plating solution for 2 min.

More experiments were performed to understand why the hydroxylamine Au plating solution did not appear to plate directly on the Au NPs used in this research. It’s known that a transition metal acts as a catalyst during the electroless plating. The reducing agent and metal ions of the electroless plating solution adsorb to the catalyst surface and the reaction takes place \[41\]. Considering that the negative charge on Au colloids could impact the adsorption of Au ions and reducing agents to the catalyst surface and thus influence the plating, 10 mM Mg\(^{2+}\) (in the forms of MgCl\(_2\) and MgAc\(_2\)) was added into the plating solution. However, the plating solution still did not plate as no height increase on the seeded DNA origami was observed. In the literature, the presence of citrate ions in this Au plating solution did not quench the plating \[111\]. Thus, it is likely that the bis(p-sulfonatophenyl) phenylphosphine dihydrate dipotassium and/or
thiolated oligonucleotides on Au NPs impacted the Au plating, perhaps by influencing the adsorption of Au ions and/or the reducing agent (hydroxylamine) on the surface of Au NPs.

There may be a few other methods to obtain more uniform plating results. For instance, if the plating reaction can be slowed down by lowering the temperature, uniform plating could be achieved. Additives (i.e. thiourea and diphenylthiourea) that can change the plating mechanism and the morphology of the plating [112] could also be used here to achieve more uniform plating.

4.1.2 Site-specific Metallization of DNA Origami for the Application in Integrated Circuits

In integrated circuits, the ability to control the location of conductive components is essential in device design. For example metal-oxide-semiconductor field-effect transistors (MOSFETs) require conductive materials in separate locations to act as the source, drain, and gate electrodes. In order to create similar geometries with DNA origami templated electrodes, locations of gaps in the metallization must be effectively controlled. Here I demonstrate that this is possible using my branched, T-shaped DNA origami. The design of the DNA origami was adjusted so that the A_{10} extension (attachment point) was added only to staple strands located towards the ends of the top branches as shown in Figure 4-18A. Before the seeding, DNA origami was diluted to 0.67 nM for the deposition on SiO_{2} surfaces. The seeding of this DNA origami was performed using the same procedures as that for seeding T-shaped DNA origami along top branches on SiO_{2} surfaces. Seeding (Figure 4-18B) and Au plating of this structure on SiO_{2} surfaces resulted in a 100 nm gap between metallized portions (Figure 4-18C-D, see Section 4.2 for experimental details on seeding and plating). This geometry could be used to
form a transistor if a semiconducting material, such as a carbon nanotube, was inserted between metallized regions.

Metallization of a template for electronic circuits was one of the ultimate goals for DNA metallization in this research. An electronic circuit could be a combination of transistors connected by metal wires. For example, if two p-type transistors are connected in parallel by metal wires as shown in Figure 4-19A, a PMOS NOR circuit is formed. The work here is to form Au nanowires on specific areas of a circuit-shaped DNA template. Thus, a circuit-shaped DNA origami template was assembled with attachment points anchored at specific places for Au seeds (Figure 4-19B).

Figure 4-18: Metallization of T-shaped DNA origami along the top branches with a gap in the middle. A) shows a schematic of the seeding geometry. B) AFM image of seeded T-shaped DNA origami where a gap is seen between seeded regions. (C) and (D) are AFM and SEM images, respectively, of the seeded, T-shaped DNA origami with a gap after Au plating. Height scale is 6 nm in (B) and 50 nm in (C). Scale bars: 100 nm.
Considering the relatively large size of this origami structure, the origami solution was diluted to 0.2 nM of origami for surface deposition. Then, the circuit-shaped DNA origami was deposited onto a SiO$_2$ surface (Figure 4-19C) and seeded on the surface with Au NPs using the same procedures as that for seeding T-shaped DNA origami on top branches. The plating on this circuit-shaped origami was allowed to proceed for only 1 min with the modified commercial plating solution so that the predesigned gaps were not filled while the spacing between Au NPs could be filled after the plating. Figure 4-19D shows that the circuit-shaped DNA origami was seeded and Figure 4-19E shows that it was plated (see Section 4.2 for experimental details) successfully at designated positions with binding sites, leaving gaps for the localization and operation of semiconductors. The plating appeared relatively continuous, which could be due to a higher density of seeding attributed from the locations of binding sites. The successful metallization of circuit-shaped DNA origami at designated sites is important progress for the fabrication of DNA-templated nanoelectronic circuits.
To conclude, continuous Au nanowires were first prepared on predesigned locations on DNA origami. Specifically, continuous metallization was achieved on top branches of T-shaped DNA origami seeded with Au NPs on a SiO$_2$ surface. The average spacing between adjacent Au NPs on origami was 5.8 nm with a median spacing of 4.1 nm, significantly smaller than the ~15 nm reported by Pais et al. [77] in a work parallel with that presented here. The smaller spacing in my work led to continuous Au nanowires with an average width of 33 nm after electroless Au
plating on a SiO$_2$ surface, smaller than the 50 nm reported recently by Pais et al. The smallest nanowires prepared here had a width of ~20 nm. If the seeding process used in this study can be further improved such that the maximum spacing between neighboring Au NPs is not greater than 4.1 nm (currently our median spacing), and the plating solution can plate uniformly, continuous nanowires with a width of 12 nm may be prepared on predesigned locations on DNA origami. In this study, I also successfully metallized circuit-shaped DNA origami at predesigned sites for the construction of DNA-templated nanoelectronic circuits. Altogether, these results represent important progress toward the realization of DNA-templated nanoelectronic circuit fabrication.

4.2 Materials and Methods

4.2.1 Materials

M13mp18 and streptavidin-coated magnetic beads were purchased from New England Biolabs. Staple strands for DNA origami folding were ordered from Operon Biotechnologies (100 μM in TE buffer). Single-stranded DNA thiol was purchased from Operon Biotechnologies with PAGE purification and diluted to 1 mM in water. PCR primers were also ordered from Operon. PCR purification kits were acquired from Qiagen. DNA polymerase and PCR buffers were purchased from Invitrogen or New England Biolabs. 30k MWCO and 100k MWCO Amicon ultra-0.5 mL centrifugal filters were obtained from Millipore. 5 nm gold nanoparticles were obtained from Ted Pella. BSPP (bis(p-sulfonatophenyl)phenylphosphine dihydrate dipotassium salt) was obtained from Strem Chemicals.
4.2.2 DNA Origami Designs

Branched (“T”) shaped DNA origami structures were formed using a 2,958 base scaffold, amplified from M13mp18 as previously reported [113]. To enable Au NP attachment, select staple strands from the previously reported design were modified to contain a sequence of 10 adenine nucleotides on the 3’ end. For conductivity measurements, the entire top branch consisted of modified staple strands (67 in total). For the “T” structure with a gap, 39 staples were modified. The prototype circuit element structure was folded using M13mp18 for the scaffold with 246 staple strands. 174 of the staple strands contain the extra 10 adenines on the 3’ end for Au NP attachment.

4.2.3 DNA Origami Folding

Both types of DNA origami structures were folded by heating a mixture of the scaffold and staple strands (2 nM scaffold and 20 nM of each staple strand in 1X TAE-Mg²⁺ buffer) to 95°C for 3 min and then slowly cooling to 4°C over 90 min. DNA origami solutions were filtered with 30 k MWCO Amicon filters, to remove most of the excess staple strands, by centrifuging for 10 min at 13,000 rpm with an Eppendorf 5415C centrifuge. Samples were rinsed twice with 500 µL 1xTAE-Mg²⁺ buffer by centrifuging for 10 min at 13,000 rpm and recovered by spinning for 3 min at 3,500 rpm.

4.2.4 Au NP Preparation

The Au NPs were phosphinated and concentrated with BSPP using procedures reported previously ([104]). More specifically, 1.5 mg BSPP was added to 5 mL of Au NPs and shaken overnight. 100 mg of NaCl was added and the solution was centrifuged to pellet the Au NPs. The
supernatant was removed and the Au was resuspended with an aqueous BSPP solution (100 µL, 2.5 mM). Methanol (100 µL) was added and the solution was centrifuged again to pellet the Au. After removing the supernatant again, the Au was resuspended in aqueous BSPP solution (100 µL, 2.5 mM). The concentration of Au NPs was estimated from the absorption at 520 nm using a Nanodrop 1000 spectrophotometer.

### 4.2.5 Au NP-S-DNA Conjugates

Thiolated DNA was ordered from Operon Biotechnologies PAGE purified and was resuspended in water. The oligonucleotide was used without deprotecting the disulfide bond as it was found that the reaction worked either with or without deprotection. Au NPs and thiolated DNA were combined in a 1:200 molar ratio and left to react at room temperature for at least 19 hours.

The Au NP DNA conjugates were filtered using 30k MWCO Amicon filters to remove unbound thiolated DNA. Samples were then rinsed twice using 0.5 X TBE buffer. About 30-35 µL was recovered, with Au NP concentrations around 3 µM. The filtered Au NP DNA conjugates can last at least 2 months when kept in a refrigerator.

### 4.2.6 Attachment of Au NP to DNA Origami in Solution

For solution attachment of Au NPs to DNA origami structures, DNA origami (10 µL, 5.7 nM) was combined with the Au NP DNA conjugates (2 µL, 2.9×10^{-7} M of Au NP) giving a ratio of ~10:1 Au NP per DNA origami structure. The solution was cooled from 37 °C to 20 °C over about 17 min. Then the solution was deposited on a surface for AFM imaging.
4.2.7 Procedure for Seeding of DNA Origami on a Mica Surface

Four microliters of DNA origami was deposited onto a mica surface and allowed to adsorb to the surface for 1 min at room temperature. Then, the surface was rinsed for 5-6 sec with 4 mM of MgAc$_2$ and 1 sec with water, followed by drying with a stream of filtered air. Then, the sample was put into a humid chamber (a plastic container with about 1 cm-deep of water with a smaller glass. Figure 4-20). Twelve microliters of seeding solution was transferred onto a mica surface and the seeding was allowed for 15 min, 30 min, or 1 hr at room temperature. After seeding, the sample was rinsed with 4 mM of MgAc$_2$ for 5-6 sec and with water for 1 sec. At last, the sample was dried with a stream of filtered air.

![Illustration of a humid container used for seeding DNA origami on a mica or SiO$_2$ surface.](image)

4.2.8 Procedure for Depositing DNA Origami onto a SiO$_2$ Surface and Seeding on the Surface

A SiO$_2$ wafer was cleaned for 30 sec in a plasma cleaner (Plasma Cleaner from Harrick Plasma, NY. PDC-32G, 100W of input power, 18W of power applied to RF coil, 8-12MHZ).
Then, 3 μL of filtered DNA origami (2 nM or 0.67 nM of origami for T-shaped origami with binding sites along top branches; 0.67 nM of origami for T-shaped origami with binding sites at both ends of top branches; 0.33 nM of origami for circuit-shaped DNA origami) was put onto the plasma cleaned SiO₂ surface and allowed to sit for 2 hours in a humid chamber at room temperature. (For investigation of the deposition process, deposition of DNA origami for 1 min, 3 min, 5 min, and 10 min was also used.) The SiO₂ surface was then rinsed in a 50% ethanol solution (5 sec) and a 90% ethanol solution (1 hour) at room temperature. Afterward, the surface was dried with a stream of filtered air and put back into the humid chamber. Subsequently, 12 μL of seeding solution (Au NPs coated with thiolated T₈ DNA in 10X TAE buffer, 12 nM) was added onto the surface and allowed to seed DNA for 30 min at room temperature. Then, the SiO₂ surface was rinsed in 10X TAE buffer (5 sec), 50% ethanol solution (5 sec), and 90% ethanol solution (1 hour). At last, the surface was dried with a stream of filtered air.

4.2.9 Electroless Au plating

The commercial Au plating solution was prepared according to the manufacturer’s instructions. This plating solution was then mixed with the same volume of MgCl₂ to yield a final Mg²⁺ concentration of 2 mM or 10 mM. The plating was conducted by putting 60 μL of plating solution onto a mica or SiO₂ sample surface at room temperature. The plating was allowed to proceed for 30 sec, 1 min, 2 min, 3 min, 5 min, 10 min, or 20 min. Then, the plating was quenched by rinsing the surface with 4 mM of MgAc₂ for a few seconds, then with water for 2 seconds. At last, the surface was dried with a stream of filtered air.

The hydroxylamine Au plating solution consists of 0.01% (weight) of HAuCl₄ and 0.001% (weight) of NH₂OH in water. For the plating, 60 μL of the hydroxylamine Au plating solution
was put onto a sample, either seeded DNA origami or DNA origami that was plated for 1 min with commercial Au plating solution, and allowed to plate for 2 min. Afterward, the surface was rinsed with 4 mM of MgAc$_2$ for a few seconds, then with water for 2 seconds and dried with a stream of filtered air.

Specifically, the T-shaped DNA origami with binding sites on the ends of the top branches, and the circuit-shaped DNA origami were only plated for 2 min and 1 min with the commercial Au plating solution (with 10 mM of Mg$^{2+}$) after seeding on a SiO$_2$ surface. No further plating was performed on these two DNA origami structures.

### 4.2.10 Calculation of Semi-infinite Diffusion

Here, I assume that the plating is diffusion limited at first. A 1-D semi-infinite model is used for the calculation. The concentration of the reactant only varies in the direction perpendicular to the surface. Then, I calculate the amount of Au diffused to the surface ($NB$) in 1 minute based on this assumption. Subsequently, the amount of Au actually deposited on the surface ($n$) in the experiment is calculated based on the number of seeds on the surface and the increase of the size of the seeds in 1 min of plating. Then, I compare $NB$ and $n$. The calculation of semi-infinite diffusion of reactants to the surface is based on

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}, t \geq 0, x \geq 0,$$

(4-1)

in which $c$ is the concentration of the reactant ($4\times10^{-5}$ mol/L), $t$ is the diffusion time (1 minute), $D$ is the diffusion coefficient of the reactant ($\sim10^{-5}$ cm$^2$/s), and $x$ is the distance from the surface. The initial condition is

$$c(x, 0) = c_0, x \geq 0,$$

(4-2)

in which $c_0$ is a constant. The boundary conditions are
\[ C(x,t) = C_0, \quad \text{when } x = \infty, \quad t > 0, \quad (4-3) \]

and

\[ C(x,t) = 0, \quad \text{when } x = 0, \quad t > 0. \quad (4-4) \]

The resulting solutions are

\[ N(0,t) = \frac{\sqrt{D}}{\sqrt{\pi t}} \cdot C_0, \quad (4-5) \]

in which \( N(0,t) \) is the flux to the surface.

\[ \frac{C}{C_0} = 1 - \text{erfc} \left( \frac{x}{2\sqrt{D}t} \right). \quad (4-6) \]

\[ NB(t) = \int_0^t A \sqrt{\frac{D}{\pi t}} C_0 \, dt = \frac{2 \cdot A \cdot \sqrt{D} \cdot t \cdot C_0}{\sqrt{\pi}}, \quad t > 0, \quad (4-7) \]

in which \( NB \) is the amount of the reactant diffused to the surface, and \( A \) is the selected surface area (2\( \mu \)m by 2\( \mu \)m). When \( t \) is equal to 1 minute, \( NB \) is equal to \( 4.42 \times 10^{-17} \) mol.

The amount of Au actually deposited onto the selected surface area can be calculated through the number of seeds in the selected area on the surface (30 seeded origami, 16 seeds per origami in an area of 2\( \mu \)m by 2\( \mu \)m), the increase of seed size after 1 minute of plating, and the density of Au. The related equations are

\[ V = 480 \cdot \frac{4\pi}{3} \cdot (R^3 - r^3), \quad \text{and} \quad (4-8) \]

\[ n = \frac{\rho \cdot V}{M} \quad (4-9) \]

in which \( V \) is the volume of Au deposited onto the surface (an area of 2\( \mu \)m by 2\( \mu \)m), \( R \) is radius of Au seeds after 1 minute of plating, \( r \) is the radius of the Au seeds before plating, \( n \) is the amount of Au deposited on the surface (in mole), \( \rho \) is the density of Au (19.3 g/cm\(^3\)), and \( M \) is the molecular weight of Au (197 g/mol). The resulting value of \( n \) (4.33\( \times \)10\(^{-17} \) mol) is approximately equal to the amount of material that would have transferred to the surface after 1 minute of Au plating under diffusion-limited conditions (\( NB = 4.42 \times 10^{-17} \) mol). Thus, the
observed Au plating rate was consistent with that expected under mass transport control. Also, we know that the concentration of the solution near the surface is significantly depleted after 1 minute of Au plating under diffusion-limited conditions, and that the flux at the surface decreases with time.
5 FABRICATION OF CONTINUOUS DNA-TEMPLATED NICKEL AND COPPER NANOWIRES AND GALVANIC DISPLACEMENT OF THEM BY TELLURIUM AND BISMUTH TELLURIDE

5.1 Introduction

After the successful deposition of Au onto DNA templates to form conductive Au nanowires, we also explored the fabrication of DNA-templated nanowires of a variety of materials for the potential applications in nanoelectronics, next-generation sensors, and plasmonics. Specifically, fabrication of continuous DNA-templated Cu, Ni, Te, and Bi$_2$Te$_3$ nanowires will be demonstrated in this chapter.

Cu is an important material used for the interconnections in the semiconductor industry because of its low electrical resistivity and high resistance to electromigration [114]. Therefore, there has been interest in preparing Cu nanowires on DNA templates [50, 115-119] for the fabrication of DNA-templated nanoelectronic circuits. However, neither SEM was used to characterize the morphology of DNA-templated Cu nanowires in the literature, nor any elemental analysis technique was used to analyze the composition of the resulted Cu nanowires [50, 115, 116, 118, 119].

Ni is a magnetic material. Ni nanowires are potential materials for applications in high-density information storage [79]. As discussed earlier in the second chapter, DNA is an excellent template for the fabrication of metal nanowires. Preparation of DNA-templated Ni nanowires has been reported in the literature Ni [60, 80]. However, conductive DNA-templated Ni nanowires
with a uniform size have never been demonstrated in the literature [60, 80]. And no conductivity test performed on DNA-templated Ni nanowires has ever been reported. In the literature, conductivity tests on DNA-templated Ag [36, 70, 71], Au [54, 67, 81], and Pd [37, 52, 56] nanowires showed that the conductivities of these nanowires were 1 to 8 magnitudes lower than that of their respective bulk materials. Ni is also an active metal, so that the fabrication of Ni nanowires on DNA templates provides the opportunity for the deposition of a variety of other materials onto DNA.

Selective deposition of semiconductor materials onto DNA templates is needed for the fabrication of DNA-templated nanoelectronic circuits. To date, semiconductors including CdS [82-84], CuS [85], CdSe [86], and CdSe/ZnS [87] have been deposited onto DNA templates. However, a few key challenges about the deposition of semiconductors onto DNA templates still haven’t been addressed. These challenges include: (1) depositing useful semiconductor materials besides CdS, CuS, CdSe, and CdSe/ZnS onto DNA templates, (2) the lack of ability to control the diameter of semiconductor nanowires, which could have a significant impact [88] on the nanowires’ physical properties, (3) obtaining good selectivity when depositing semiconductor materials onto DNA templates, and (4) doing the whole process in a relatively fast manner. One method that could simultaneously address all these challenges is galvanic displacement.

Tellurium (Te) and bismuth telluride (Te$_2$Bi$_3$) are both semiconductor materials [93, 97]. Te has applications in electronics, piezoelectric devices, high-efficiency photoconductors, and carbon monoxide and ammonia gas sensors [94, 120-123]. Moreover, Te and its alloys are considered important semiconductor materials for thermoelectric generators and coolers [94]. Bismuth telluride (Bi$_2$Te$_3$) and its alloys are known as the best bulk thermoelectric materials [124, 125]. Since its discovery, Bi$_2$Te$_3$ has become very important for the thermoelectric industry [125].
Compared to the bulk material, 1D nanostructures are predicted to have a significantly higher thermoelectric figure of merit [96, 126, 127] due to decreased thermal conductivity through phonon scattering in the 1D nanostructures. Thus, the fabrication of 1D Te and Bi$_2$Te$_3$ nanostructures is also of great interest for the thermoelectric industry [94]. Galvanic displacement has been used to make a variety of metal and semiconductor nanostructure materials [89, 90, 92-96, 128]. Specifically, Te and Te$_2$Bi$_3$ can galvanically displace electrodeposited nickel and cobalt, as shown in the literature [94-96].

In this chapter, continuous Ni and Cu nanowires are successfully fabricated on a $\lambda$-DNA template through Ag seeding and electroless Ni and Cu plating. Conductivity tests performed on DNA-templated Ni nanowires show that they are conductive. The smallest, continuous Ni nanowires fabricated here are as narrow as 28 nm. Then, these metal nanowires are converted to tellurium (Te) or bismuth telluride (Bi$_2$Te$_3$) nanostructures through a galvanic displacement reaction.

5.2 Results and Discussion

$\lambda$-DNA was seeded using a method modified from the literature [36]. First, $\lambda$-DNA was aligned on an octyldimethylmonochlorosilane ($C_8$DMS) passivated SiO$_2$ surface [Figure 5-1A] (see Section 5.3.2 for experimental details) and then immersed in silver ammonia solution for 5 min, during which complexed silver ions attached to negatively charged DNA scaffold through a combination of electrostatic interaction and complex formation with DNA bases [36]. Subsequently, the surface was dried with a stream of filtered air. The silver ions associated with the DNA were then reduced by hydroquinone for 2 min to form metallic Ag nanoparticles on the DNA template. The seeding process was performed twice to enhance the seeding density. The
Ag nanoparticles [Figure 5-1B] on λ-DNA were then used to catalyze electroless deposition of Ni and Cu on the DNA template to form metallic nanowires.

Figure 5-1. AFM images of λ-DNA before (A) and after (B) Ag seeding on a silanized SiO₂ surface. Height scale is 6 nm in (A) and 25 nm in (B).

A double stranded λ-DNA molecule is about 16 µm long. When aligned on a hydrophobic silane monolayer on silicon wafer, it can form DNA bundles, as seen in Figure 5-1A, which can be more than 20 µm long. Figure 1B shows an AFM image of Ag seeded λ-DNA after seeding twice. It can be seen that DNA was selectively seeded, although the Ag seeding on the DNA was not continuous (zoom-in image in Figure 5-1B). The discontinuous seeds can serve as catalysts for electroless plating and form continuous nanowires after plating. After seeding twice, the average height of seeded part of DNA was 12.5 nm with a standard deviation of 3.2 nm (n=51). Compared with other Ag seeding methods in the literature, such as using glutaraldehyde to modify DNA [66-71, 129], this Ag seeding method takes much less time (less than 20 minutes) and can still seed DNA with relatively high density and good selectivity.

In order to plate Ni on Ag seeds, an electroless Ni plating bath consisting of 30 g/L NiCl₂·6H₂O, 0.7 g/L NaBH₄, 60 g/L NH₂(CH₂)₂NH₂, and 40 g/L NaOH (pH=13, T=95°C) [130]
was used. It was found that the plating solution (either with or without reducing agent) will displace Si, even with the native SiO₂ layer and the silane layer on the surface. Thus, a Si wafer with a thermal SiO₂ layer of 500 nm was used as the substrate for the preparation of DNA-templated Ni nanowires. Electroless plating of nickel on the Ag seeded λ-DNA samples was performed at 82 °C and it was found that most of the DNA was removed from the surface during plating (Figure 5-2; compare with Figure 5-1B). It is believed that the DNA removal was due to the relatively high temperature and to bubble formation during plating [131].

![AFM image of Ag seeded λ-DNA after 2 min of electroless Ni plating at 82 °C. Height scale: 30 nm.](image)

To keep Ag-seeded λ-DNA on the surface during electroless Ni plating, the operating temperature of plating solution was lowered. After 5 min of electroless Ni plating at 70°C, seeded DNA was observed to remain on the surface. However, no significant height change due to the plating was observed. This was undoubtedly due to the slower plating rate at the lower temperature. To offset this effect, the concentration of the reducing agent (NaBH₄) in the electroless Ni plating solution was increased by a factor of 3. Plating of Ag seeded λ-DNA at
70 °C was performed with this modified solution for 2 minutes. AFM imaging of the resulting sample showed that the λ-DNA templates were plated with an average height of 41 nm (Figure 5-3A). SEM images [Figure 5-3B-F] have confirmed that continuous nanowires were formed after electroless Ni plating. The nanowires formed consist of multiple grains which likely grew from non-continuous Ag seeds on DNA templates. When plated for 2 min [Figure 5-3B&C], the average width of the nanowires formed was 38 nm, with narrowest nanowires having a width of 28 nm when plated at this condition. The variation of the width among different nanowires could be due to the fact that single DNA molecules and DNA bundles are seeded with different seed sizes and densities. For instance, DNA bundles could seed better than single molecules because of the higher density of nucleation sites and negative charge [85, 132]. Some of the resulting nanowires are not continuous when plated for 2 min, which are likely due to the relatively large spacing between adjacent seeds at some locations. This would require additional plating in order to form a continuous wire. The length of continuous nanowires was typically less than 3 μm when plated for 2 min. Electroless Ni plating for 4 min [Figure 5-3D-F] resulted in wires with widths of approximately 100 nm. SEM images of the wires clearly show that they are composed of distinct grains (see e.g, Figure 5-3D&F). Many of the continuous nanowires have a length greater than 10 μm, much longer than those plated for 2 min (3 μm). This is because that the longer plating time allows the bridging of gaps that still existed on the nanowires plated for only 2 min. The nanowires are uniform with a ratio of standard deviation to average width equal to 0.06. Later in this chapter, it is calculated that the Cu plating (on Ag seeded λ-DNA) operates at or near the diffusion limit. This Ni plating solution consists of ions of similar or higher concentrations ([Ni^{2+}] = 0.126 M, [NaBH₄] = 0.056 M; [Cu^{2+}] = 0.02 M, [HCHO] =0.123 M), however, the rate of Ni plating is more than one order of magnitude lower than that of Cu plating.
Thus, the Ni plating is likely kinetically controlled. This is why uniform plating was achieved on different seeds. The fabrication of uniform (same width along one single nanowire) DNA-templated Ni nanowires is a significant improvement from the literature, in which the width of the same nanowire varied significantly at different sites [60]. EDX analysis [Figure 5-3G] performed on a Ni nanowire (plated for 4 min) confirmed the presence of Ni. The Ag peak was not seen on EDX, which could be due to the small size of Ag nanoparticles (compared to 1 micron, the magnitude of penetration depth of electrons used in SEM) so that the produced signal was in the noise level. Figure 5-3A-F show some background deposition on samples plated for both 2 min and 4 min; however, the nanowires are easily distinguished. I attribute the background deposition to Ag seeds deposited on the background from the seeding step as no background deposition was found on control plating experiments prior to seeding. Figure 5-3H shows an AFM image of C₈DMS silanized, blank (non-seeded) SiO₂ after 4 min of electroless Ni plating at 70 °C. The surface was very clean after plating without any solution decomposition.

Earlier, I also did the same seeding and electroless Ni plating on λ-DNA aligned on an octadecyldimethylmonochlorosilane (C₁₈DMS; see Section 5.3.3 for experimental details) passivated, thermally grown SiO₂ surface (500 nm SiO₂ on a Si wafer). The resulting Ni nanowires (Figures 5-3I&J, plated for 2 and 4 min) display morphologies very similar to these prepared on the C₈DMS passivated, thermally grown SiO₂ surface (see last paragraph). Later, I found that the seeding of DNA on the C₁₈DMS passivated, thermally grown SiO₂ surface was not very reproducible although it was still very reproducible on the C₁₈DMS passivated, native oxide on the silicon wafer and on the C₈DMS passivated, thermally grown SiO₂ surface. It’s believed that the thermal oxidation process for producing SiO₂ has changed some property of the silicon wafer surface, thus impacted the growth of C₁₈DMS layer on the top and influenced the Ag
seeding of λ-DNA. Although my conductivity tests (presented later in this chapter) were performed on the Ni nanowires that had been prepared on the C₁₈DMS passivated, thermally grown SiO₂ surface, I believe that they can also represent the conductivity of the Ni nanowires prepared on the C₈DMS passivated, thermally grown SiO₂ surface because these nanowires (made on C₈DMS or C₁₈DMS on thermally grown SiO₂) were prepared through the same seeding and plating process, and displayed very similar morphologies as appeared on SEM images.

Mixed potential theory can be used to explain how the increase of the reducing agent led to the faster plating. Figure 5-4 shows that the plating reaction occurs at the mixed potential, where the anodic reaction and cathodic reaction lines cross. With the original concentration of reducing agent, the mixed-potential of the plating solution was V, and the current exchanged in cathodic or anodic reaction was I_{mix}. When the concentration of reducing agent increased by a factor of 3, the cathodic reaction line didn’t shift; however, anodic reaction line shifted to the left (see dotted line in Figure 5-4) because the concentration change impacted the anodic electrode potential, according to Nernst equation [133]. Therefore, mixed potential shifted to V’ and greater current (I_{mix’}) and higher plating rate was achieved, due to the change of overpotentials of anodic and cathodic reactions.
Figure 5-3: AFM (A) and SEM (B & C) images of Ag-seeded λ-DNA templates following Ni plating for 2 min at 70°C on the C₈MDS silanized, thermally grown SiO₂ surface. AFM height scale: 80 nm. (D – F): SEM images of Ag seeded λ-DNA after 4 min of electroless Ni plating at 70°C on the C₈MDS silanized, thermally grown SiO₂ surface. G: EDX analysis performed on a Ni nanowire (plated for 4 min) using the spot scan. H: AFM image of a control sample after 4 min of electroless Ni plating on a blank (non-seeded) C₈MDS silanized, thermally grown SiO₂ surface. Height scale: 6 nm. (I&J) SEM images of Ag seeded λ-DNA after 2 min and 4 min of electroless Ni plating at 70°C on the C₁₈MDS silanized, thermally grown SiO₂ surface, respectively.
Conductivity tests were performed on the DNA-templated Ni nanowires (plated for 4 min) on the C$_{18}$DMS silanized thermal SiO$_2$ surface. Electron beam lithography was used to pattern Au pads onto the SiO$_2$ surface after the fabrication of Ni nanowires [Figure 5-5A]. A 340 nm-wide gap was fabricated between two adjacent pads [Figure 5-5B-D]. The conductivity of nanowires across these two pads was then measured by applying voltages to the pads and collecting the currents.

Figure 5-4: Analysis of plating rate with mixed-potential theory. C: concentration of the reducing agent.
Figure 5-5: Zoom out (A) and zoom in (B-D) SEM images of Au pads on Ni nanowires (on the C\textsubscript{18}MDS silanized, thermally grown SiO\textsubscript{2} surface) fabricated by e-beam lithography for two-terminal conductivity tests. (E): Linear I-V plots show ohmic behavior of DNA-templated Ni nanowires in image (C). (F): Measured electrical resistances of 17 devices. Red, blue, and green represent devices with 1, 2, and 3 continuous nanowires across the gap, respectively.
Conductivity tests were performed on devices with between one and three continuous Ni nanowires across the gap. The results of conductivity tests indicated ohmic behavior of Ni nanowires. For example, the current and voltage measured from the device in Figure 5-5C displayed a linear relationship (Figure 5-5E). Results from 17 devices (Figure 5-5F) show that the resistance roughly decreases with the increased number of continuous nanowires across the gap. Four out of five of the devices with resistances greater than 5,000 Ω had just one continuous nanowire across the gap. The resistance of devices with one continuous nanowire across the gap varied from 12,726 Ω to 1,323 Ω, likely due to the varied continuity of the nanowires. The resistances of the six devices that contained three continuous nanowires were not greater than 1,062 Ω. For the calculation of the resistance of each individual nanowire, we assume that the nanowires across the same gap of one device have the same resistance. Then, the resulted resistance of nanowires (a total of 33) from these 17 devices ranged from 666 Ω to 31,376 Ω. Since the resistance of these varied significantly, the median value was used to represent the resistance of these Ni nanowires. The median electrical resistance of the Ni nanowires was 2,500 Ω. The resistivity of Ni nanowires ranged from 1.0×10⁻⁵ to 4.8×10⁻⁴ Ω-m, with the median value of 3.9×10⁻⁵ Ω-m. Compared to the electrical resistivity of bulk Ni (6.9×10⁻⁸ Ω-m), the measured value is about 2-4 orders of magnitude higher.

The higher measured resistivity of Ni nanowires is likely due to the combined effects of an oxide film on the Ni, and both surface and grain boundary scattering. Surface and grain boundary scattering is known to increase the resistivity of nanowires significantly, as reported in the literature [51, 54, 134]. This increase could be more than an order of magnitude. Second, the thin oxide layer formed on Ni under ambient conditions (room temperature; in air), while protecting the inside of Ni nanowires from being oxidized, also increases the measured resistivity.
of Ni nanowires since it is located between the Au pad and the Ni nanowire(s). Kulpa et al. [135] reported that the maximum oxide film formed on electroplated nickel at room temperature and a relative humidity up to 95% was smaller than 2.3 nm. The film thickness oxide didn’t increase after 111 hrs of exposure to the air. Thus, the oxide layer formed on these DNA-templated Ni nanowires stored in our lab (room temperature, relative humidity < 50%) shouldn’t be greater than 2.3 nm. If the resistivity of the native nickel oxide layer is more than 2 orders of magnitude higher than that of Ni (quite possible), the resistance of the nickel oxide layer on the Ni nanowire will be significant. The decrease of the cross Section area of metallic Ni (due to the formation of oxide) would also increase the electrical resistance of the Ni nanowires. This increase will have a more significant impact on the smaller nanowires than on larger nanowires. However, this impact is not significant in our system here. For example, a decrease of 2.3 nm in surface layer of the nanowires of 28 nm, 100 nm in width would only increase the electrical resistance of the nanowires by about 23% and 7%, respectively. Contact resistance includes (1) the resistance between the Au pad and nanowires and (2) the resistance from the contact between the Au pad and the micromanipulator needle. The contact resistance might also increase the measured electrical resistance; however, we believe it is a very small increase. As reported by Keren et al. [67], the overall resistance of a DNA-templated Au nanowire (a few micrometers long, 50-100 nm wide) was about 25 Ω when measured using the two-terminal method with Au pads deposited on nanowires. In this research, Au pads were also fabricated on the nanowires with a similar size, so it’s expected that the contact resistance between the pad and nanowires should be smaller than 25 Ω. The resistance due to the contact between micromanipulator needle and the Au pad, together with the resistance of micromanipulator needle, and the resistance of Au pad in our system is less than 10 Ω. The conductivity tests performed here prove that DNA-templated
Ni nanowires fabricated in this work are conductive, providing opportunities for preparing nanowires of a variety of materials on DNA template through galvanic displacement reactions. These conductive Ni nanowires also have potential applications in high-density information storage.

As mentioned above, the fabrication of 1D Te nanostructures is of great interest [94]. Here, DNA-templated Ni nanowires prepared on the SiO$_2$ surface were converted to Te nanostructures at room temperature through a galvanic displacement reaction [94]. The galvanic displacement of Ni by Te has been reported by Rheem et al. [94]. The Ni nanowires (with diameters of 70 nm, 120 nm, 220 nm) used in their report were fabricated by electrodeposition using polycarbonate membranes as nanotemplates. The displacement of the whole Ni nanowire can be explained in Figure 5-6. During the beginning of the galvanic displacement reaction, the surface of Ni nanowires was displaced and an incomplete layer of Te was formed. Then, the reactants diffused through pores in the surface layer and displaced the Ni on the inside of the nanowires. Ni ions (Ni$^{2+}$) produced in the displacement reaction diffused into the displacement solution through the pores and were removed in the rinsing step after 2 hours of displacement.

The displacement reaction took place according to reactions (5-1) and (5-2). The solution for the Te-displacement reaction consisted of 0.01M TeO$_2$ and 1M HNO$_3$. Figure 5-7A&B display SEM images of DNA-templated Ni nanowires (plated for 4 min) before (Figure 5-7A) and after (Figure 5-7B) 2 hours of Te-displacement. The nanowire after Te displacement reaction did not look as granular as it did prior to the displacement reaction. The contrast of SEM images of the wires was also different after displacement, where the brightness of the the nanowires relative to the background (Figure 5-7A) was less than that observed for the wires prior to displacement (Figure 5-7B). EDX analysis (Figure 5-7C) performed on the Te nanowire in
Figure 5-7B using the spot scan feature on an SEM (Philips XL30 ESEM FEG) confirmed the presence of Te and disappearance of Ni as a result of the reaction. The width of the Te nanowire was about 100 nm, the same as that of the Ni nanowire. However, the 100 nm wide Te nanowire is unexpected. From equation (1) and (2), 1 mol of Te can displace 2 mol of Ni. Considering the molecular weights and bulk densities of Ni and Te, a solid, nonporous Ni nanowire of 100 nm diameter will be replaced by a solid, nonporous Te nanowire of 125 nm diameter. With the presence of pores, the diameter of Te nanowires should be greater than 125 nm. It is possible that the smaller Te nanowires (100 nm wide) obtained after the displacement reaction were due to dissolution of the deposited Te in HNO₃ (reaction 5-3) [136-138]. To further confirm the dissolution of Te nanowires in the displacement solution consisting of nitric acid, the displacement reaction was allowed to proceed for 4 hours on Ni nanowires initially 100 nm in width. Then, the width of Te nanowires obtained after the reaction was reduced further to about 60 nm (Figure 5-7D), which confirms the previous assumption. Thus, the timing of the displacement reaction is important for controlling the size of Te. Te displacement reaction performed on smaller Ni nanowires (plated for 2.5 min; 50 nm wide; Figure 5-7E) for 2 hours led to Te nanowires of 50 nm in width (Figure 5-7F). The Te nanowires obtained after the displacement reaction (Figure 5-7B&E) appeared porous; however, the porosities of these nanowires are not known due to the limited data collected. The Te-displacement reaction is very selective, occurring only on places with Ni. The selective displacement provides an opportunity to deposit materials onto DNA templates with high precision.
Scheme of Galvanic Displacement

Figure 5-6 Scheme of galvanic displacement of Ni by Te.
Figure 5-7: Ni nanowires of 100 nm in width before (A) and after (B) 2 hours of Te displacement reaction. The contrast and morphology of nanowires in these two images are different. (C) EDX analysis performed on the nanowire in image (B) using spot scan. (D) Ni nanowires of 100 nm in width after 4 hours of Te displacement reaction. Ni nanowires of 50 nm in width before (E) and after (F) 2 hours of Te displacement reaction.

\[
\begin{align*}
\text{Ni}^{2+} + 2e^- & \rightarrow \text{Ni} ; \quad E^\theta = -0.250 \text{ V} \quad \text{SHE} \\
\text{HTeO}_2^+ + 3\text{H}^+ + 4e^- & \rightarrow \text{Te} + 2\text{H}_2\text{O} ; \quad E^\theta = 0.551 \text{ V} \quad \text{SHE} \\
3\text{Te} + 7\text{H}^+ + 4\text{NO}_3^- & \rightarrow 3\text{HTeO}_2^+ + 4\text{NO} + 2\text{H}_2\text{O} 
\end{align*}
\]
DNA-templated Ni nanowires were also converted to Bi$_2$Te$_3$ nanostructures through a galvanic displacement reaction. The galvanic displacement of Ni by Bi$_2$Te$_3$ was first demonstrated by Xiao et al. [96]. The Ni nanowires used in their report were prepared by electrodeposition using polycarbonate membranes as nanotemplates. The overall displacement reaction was described as follows [96]:

$$2\text{Bi}^{3+} + 3\text{HTeO}_2^+ + 9\text{Ni} (s) + 9\text{H}^+ \rightarrow \text{Bi}_2\text{Te}_3 (s) + 9\text{Ni}^{2+} + 6\text{H}_2\text{O}$$  (5-4)

Here, a similar solution was used to displace my DNA-templated Ni nanowires with Bi$_2$Te$_3$. The solution consisted of 0.01M TeO$_2$, 0.006–0.01M Bi(NO$_3$)$_3$, and 1M HNO$_3$. The Bi$_2$Te$_3$-displacement reaction was allowed to proceed at room temperature for 2 hours. After the displacement reaction, sample morphology was characterized by SEM. EDX analysis was used to investigate the composition of nanowires after the displacement reaction.

Collecting enough X-ray signals by SEM/EDX from a small nanowire is difficult due to the large penetration depth (~1 μm) of SEM. According to reaction (5-4), only 1 mole of Bi will be produced from 4.5 mole of Ni. Thus, it would be particularly hard to detect the amount of Bi in small Bi$_2$Te$_3$ nanowires. Consequently, we prepared 500 nm wide DNA-templated Ni nanowires for the Bi$_2$Te$_3$ displacement reaction. These large Ni nanowires were seeded in the same method as described earlier in the chapter and plated using an electroless Ni plating solution that plated very fast. This Ni plating solution consisted of 0.1M of sodium sulfate, 0.01M of dimethylamineborane, 0.2M of sodium citrate, and 0.5M of boric acid. The pH was adjusted to 7 and the plating temperature was 70 °C [139]. Figure 5-8 shows the DNA-templated Ni nanowires after Bi$_2$Te$_3$ displacement reaction with the solution containing 0.01M Bi$^{3+}$. The morphology of Bi$_2$Te$_3$ formed after the displacement reaction was quite different from that of Ni nanowires, with the crystal structure of Bi$_2$Te$_3$ clearly shown [Figure 5-8]. It’s found that the
concentration of Bi\(^{3+}\) has an impact on the final composition of the displacement reaction product. When the concentration of bismuth ion was 0.006M, 0.008M, and 0.01M, the molar ratio of Te to Bi after the displacement reaction was 2.4, 2, and 1.5, respectively. The expected molar ratio of Te/Bi for pure Bi\(_2\)Te\(_3\) is 1.5. No Te/Bi binary phase with a Te/Bi molar ratio higher than 1.5 is known [140]. In the work by Stacy et al. [140] on the electrodeposition investigation of Bi\(_2\)Te\(_3\), the high Te/Bi ratio (higher than 1.5) was attributed to the excess Te in the deposit. In this research, the high Te/Bi ratio (higher than 1.5) deposit obtained using low concentrations of Bi\(^{3+}\) could also due to the coexistence of Te and Bi\(_2\)Te\(_3\) in the deposit after displacement reaction. No morphology differences were observed from nanowires with different Te/Bi ratios (2.4, 2, and 1.5). In an earlier report by Stacy [141], the formation of electrodeposited Bi\(_2\)Te\(_3\) under low overpotentials was proposed to take place in two steps. The first step is reaction (5-2). In the second step, elemental Te reacts with Bi\(^{3+}\) to form Bi\(_2\)Te\(_3\):

\[
3\text{Te} + 2\text{Bi}^{3+} + 6\text{e}^- \rightarrow \text{Bi}_2\text{Te}_3; \quad E^\theta = 0.45 \text{ V} \quad \text{SHE}
\]  

(5-5)

This mechanism can also be used to explain the results in my work. Reactions (5-5) and (5-2) are not only reactions in series, but also competing reactions (both of them need extra electrons to react). With a higher concentration of Bi\(^{3+}\), the rate of reaction (5-5) was accelerated relative to reaction (5-2), so that all of the Te produced from the first step was converted to Bi\(_2\)Te\(_3\). With a lower concentration of Bi\(^{3+}\), the rate of reaction (5-5) was not adequate to convert all of the Te produced from the first step to Bi\(_2\)Te\(_3\) before the Ni (electron source) was consumed. Therefore, the ratio of Te/Bi in the deposit at this condition was greater than 1.5 since it consisted of both Bi\(_2\)Te\(_3\) and excess elemental Te produced from reaction (5-2).
Figure 5-8: SEM images of Bi$_2$Te$_3$ nanowires obtained after immersing DNA-templated Ni nanowires into a solution consisting of 0.01M HTeO$_2$-, 0.01M Bi$^{3+}$, and 1M HNO$_3$ for 2 hours at room temperature.

As mentioned above, the preparation of continuous Cu nanowires on DNA templates is of interest for the fabrication of DNA-templated nanoelectronic circuits. In this study, I used Ag seeding and electroless Cu plating to prepare DNA-templated Cu nanowires. The electroless Cu plating solution [142] used here consisted of 5 g/L CuSO$_4$·5H$_2$O, 25 g/L KNaC$_4$H$_4$O$_6$·4H$_2$O, 7 g/L NaOH, and 10 g/L 37% HCHO. The plating experiments were performed at 65°C. Unseeded silicon wafers with native oxide upon which a C$_{18}$ monolayer had been deposited were found to be stable in the Cu plating solution, as evidenced by the absence of plating observed during 4 minutes of exposure to the plating solution [Figure 5-9]. Consequently, this surface was used for the preparation of DNA-templated Cu nanowires. λ-DNA was aligned on the surface and seeded with use of the same Ag seeding procedure described in Section 5.3.5. Subsequently, the seeded samples were plated by exposing the surfaces to the electroless Cu plating solution for 1 to 3 min in a water bath at 65°C (see Section 5.3.6 for experimental details). When plated for 1 min (Figure 5-10A), no continuous nanowires were found on the surface. After 3 min of Cu plating (Figure 5-10B), continuous nanowires with an average width of about 500 nm were observed. An SEM image of a sample plated for 3 min taken at a high magnification (Figure 5-
10C; 25590x) shows clearly the morphology of the DNA-templated Cu nanowire. The width varies at different places of the same Cu nanowire; the size of plated Cu particles on the background also varies significantly. The rate of growth after 1 min of plating was estimated as about 0.0055 mol/(m$^2$·min) by calculating the amount of deposition on the surface after 1 min of plating. The initial rate of growth of Cu on Ag within 1 min was much slower than this rate, which could be due to the difficulty of the nucleation of Cu on Ag seeds. A comparison of the observed growth rate with the rate expected under diffusion control indicates that this system likely operates at or near the diffusion limit after 1 min of plating. The factor that Cu nanowires (plated for 3 min) are much larger than Ni nanowires (plated for 4 min) is believed to be due to mass transfer controlled process for Cu plating. The method developed here for the fabrication of continuous Cu nanowires could be used for DNA-templated nanoelectronics. Since Cu is relatively reactive, the fabrication of continuous Cu nanowires also provides opportunities for preparing continuous nanowires of diverse materials.

Figure 5-9: AFM image of 4 mins of Cu plating on a blank native oxide surface on a silicon wafer. Height scale: 10 nm.
Figure 5-10: SEM images of Ag seeded λ-DNA after 1 min (A) and 3 min (B & C) of electroless Cu plating at 65°C. (D): Cu nanowires of sample C after 2 hrs’ of Te-displacement reaction. (E&F) EDX analysis performed on the nanowires in image C and D, respectively.

The standard electrode potentials of Cu^{2+}/Cu (reaction 5-6) and HTeO_{2}^{+}/Te (reaction 5-2) indicate that it should be possible to galvanically displace Cu to form Te (equation 5-7). As is known, Cu is a material well investigated and has a variety of applications in the industry. For instance, electroplated Cu is used for filling high aspect ratio-trenches for interconnects in the semiconductor industry. Te also has been used for electronics and in the solar industry. For instance, Te alloys could be used in Ovonic Unified Non-volatile Memory, which can switch
rapidly [143]. But, the deposition of Te is not studied as well as that of Cu. The displacement of Cu by Te may provide a novel method for the deposition of Te for industrial applications. Nonetheless, to my knowledge, the displacement of Cu by Te has never been reported. Here, the conversion of DNA-templated Cu nanowires to Te nanostructures by galvanic displacement was studied.

\[
\begin{align*}
\text{Cu}^{2+} + 2e^- & \rightarrow \text{Cu}; \quad E^0 = 0.342 \text{ V SHE} \\
U & = 0.551 \text{ V} - 0.342 \text{ V} > 0
\end{align*}
\]

(5-6) (5-7)

The Te-displacement reaction was performed in a solution consisting of 0.01M of TeO\(_2\) and 1M HNO\(_3\) at room temperature. Figure 5-10D shows an SEM image of the Cu nanowire after 2 hrs of displacement by Te. The morphology of the Cu nanowire before (Figure 5-10C) and after (Figure 5-10D) Te-displacement was quite different. The difference in morphology could be due to the different crystal and grain structures between Cu and Te. EDX analysis (Figure 5-10E) performed before the displacement showed a strong Cu peak, which was replaced almost entirely by a Te-peak that appeared as a result of the reaction (Figure 5-10F). The rate of the Te displacement reaction on Cu is faster than that on Ni. The reason to the faster Te displacement reaction on Cu than on Ni is not known, but it could be due to the differences in the composition and the crystal structure of Ni and Cu.

Thermodynamically, it’s also possible to displace Cu with Bi\(_2\)Te\(_3\). Thus, experiments were also performed to convert DNA-templated Cu nanowires to Bi\(_2\)Te\(_3\) nanowires. After 2 hours of displacement at room temperature in a solution consisting of 0.01M HTeO\(_2^+\), 0.006M Bi\(^{3+}\), and 1M HNO\(_3\), the morphology of Cu nanowires changed [Figure 5-11A]. On the same sample, I also found resulted nanowires with the morphology similar to that shown in Figure 5-10D. EDX analysis [Figure 5-11B] performed on the nanowire after displacement confirmed the disappearance of Cu and the presence of Te. However, no evidence of Bi was found in the EDX
results. The lack of Bi in the deposit may be due to a slow rate of reaction between elemental Te and Bi$^{3+}$ since the driving force for reaction (5-5) is considerably less on Cu than on Ni. This is supported by cyclic voltammogram data reported by Penner et al. [144] who observed that the formation of Bi$_2$Te$_3$ on highly oriented pyrolytic graphite (HOPG) electrodes started at about 0.24 V (vs. SHE, Figure 5-12) in a solution consisting of of 0.001 M TeO, 0.0015M Bi$^{3+}$, and 1M HNO$_3$. In contrast, Te deposition in a solution consisting of 0.001 M TeO and 1M of HNO$_3$ was observed to begin at about 0.29 V (vs. SHE) [144], a potential higher than that of Bi$_2$Te$_3$. In my system with a higher molar ratio of Te/Bi in solution and a different substrate (silicon dioxide), this potential difference could be greater. Although difficult, it may be possible to achieve displacement of Cu by Bi$_2$Te$_3$ with use of a solution with a much lower concentration of HTeO$_2^+$ and a much higher concentration of Bi$^{3+}$ for the displacement reaction.

![Figure 5-11](image)

Figure 5-11: (A) SEM image of the Cu nanowire after 2 hrs of Bi$_2$Te$_3$ displacement reaction at room temperature. (B) EDX analysis performed on the nanowire in (A) using spot scan.
To conclude, I developed an efficient method to fabricate uniform and conductive DNA-templated Ni nanowires. To accomplish this, it was necessary to adjust the composition of the electroless plating bath to permit deposition at milder conditions in order to be able to keep and plate Ag-seeded DNA on a silanized SiO₂ surface. The conductivity of these DNA-templated Ni nanowires was 3 magnitudes lower than that of bulk Ni, comparable to difference in conductivity between the bulk conductivity and the nanowire conductivity observed for DNA-templated noble metals (Ag, Au, and Pd) [36, 37, 52, 54, 56, 67, 70, 71, 81]. This is the first time of which I am aware that conductive nanowires of a non-noble metal have been fabricated from a DNA
template and electrically characterized. Additionally, a new method for the preparation of continuous DNA-templated Cu nanowires was developed. These Cu nanowires were fabricated using Ag seeding and electroless Cu plating, and may be useful for the fabrication of DNA-templated nanoelectronic circuits. In addition, I have successfully demonstrated a galvanic displacement method for the fabrication of DNA-templated semiconductor nanowires. The galvanic displacement method provides opportunities to deposit a variety of materials that haven’t been (or couldn’t be) deposited onto DNA through other methods. Using this galvanic displacement method, continuous DNA-templated Te and Bi$_2$Te$_3$ nanowires have been fabricated in simple processes. Among other things, these Te and Bi$_2$Te$_3$ nanowires may be useful for thermoelectrical applications. In addition, it may be possible to use the galvanic displacement method demonstrated here to make DNA-templated nanowires of a variety of other semiconductors and metals such as Ge, Ag, Au, Pt, and Pd with good selectivity.

5.3 Materials and Methods

5.3.1 Materials

The λ-DNA (in 10 mM Tris-HCl, with 1 mM EDTA, pH 8.0; Cat. No.: LS01203) used in the study was from Worthington Biochemical Corporation. It was diluted 10 times in TE buffer (10 mM Tris-HCl, 1 mM EDTA, pH=8.0). AgNO$_3$, KNaC$_4$H$_4$O$_6$·4H$_2$O (99.0%), CuSO$_4$·5H$_2$O (99.1%), HCHO (37.4%), NH$_3$H$_2$O (28%-30% as NH$_3$), H$_2$O$_2$ (30% solution), and H$_2$SO$_4$ (98%) were obtained from Mallinckrodt Baker, Inc. NH$_2$(CH$_2$)$_2$NH$_2$ was purchased from EMD Chemicals. NaOH (97%) was obtained from Spectrum Chemical Mfg. Corp. NiCl$_2$·6H$_2$O was purchased from Fisher Scientific Inc. Alcohol (200 proof) was purchased from Decon. Labs, Inc.
C$_{18}$DMS (95%), NaBH$_4$ (98%), TeO$_2$ (99+%), acetone (≥99.5%, A.C.S. reagent) and Bi(NO$_3$)$_3$ 5H$_2$O (99.99% metals basis) were purchased from Sigma-Aldrich, Inc. Octyldimethylchlorosilane (C$_8$DMS) was purchased from Gelest Inc. The water bath used for electroless Ni plating and electroless Cu plating in this research was purchased from VWR International (Type: 89032-216). The brand of oven is LAB-LINE (LR 19314). Plasma cleaning was performed with an instrument from Harrick Plasma, NY (PDC-32G, 100W of input power, 18W of power applied to RF coil, 8-12MHZ). All water (except for the water bath) used in this research was purified with use of a Barnstead EASYpure UV/UF system (Barnstead│Thermolyne Corporation) and had a resistivity of 18.3 MΩ-cm.

5.3.2 Silanization of the Oxidized Silicon Wafer with C$_8$DMS

This procedure was modified from that reported in the literature [13]. Small Sections of an oxidized silicon wafer (1cm x 1cm) were cleaned in a plasma cleaner for 30 seconds to remove any contaminants on the surface. Then, each piece of wafer was put into a glass vial (20 mL volume; about 25 mm in diameter and 50 mm in height) and sufficient C$_8$DMS (liquid at room temperature) was added to cover the surface of each wafer. The cap was then put tightly on each glass vial after adding the silane. Afterward, the glass vials were put into an oven at 70 °C for 10 min. Subsequently, these vials were taken out of oven and allowed to cool down in air (took about 10-15 min). Finally, the wafers were taken out of the vials (with a tweezer) and rinsed with acetone and ethanol for 5 seconds each by spaying the solvent on the surface, and dried with a stream of filtered air.
5.3.3 Silanization of the Oxidized Silicon Surface with C\textsubscript{18}DMS

This procedure was modified from that reported in the literature [80]. An oxidized (either thermally grown oxide or native oxide) silicon wafer (n-type, (100), prime wafer; Silicon Wafer Enterprises, LLC.) was cleaned using a piranha solution (a mixture of 98\% sulfuric acid and 30\% \text{H}_2\text{O}_2 \text{ at a volume ratio of 7:3, extremely dangerous}) at 130 °C for 10 minutes. Then, the silicon wafer was rinsed with water. This rinsing process was done as follows: after dumping the piranha solution, plenty of water was added into the container with the wafer; this rinsing step was repeated for 3 times to remove extra piranha solution; then, the wafer was taken out of the container and rinsed with water for more than 30 seconds by spraying water on the front and back sides of the wafer. After rinsing, the wafer was dried with a stream of filtered air (the humidity of filtered air used in this research was about 28\%). Subsequently, the oxidized silicon wafer was placed into a 140 mm-diameter (15 mm in height) glass container and put into an oven at 120 °C for 5 min to remove the water layer on the surface. Then, a small, open glass vial (15 mm in diameter, 15 mm in height) containing 180 mg of C\textsubscript{18}DMS was put beside the Si wafer. Afterward, a 125 mm-diameter glass container was put upside down on the 140 mm-glass container to cover the wafer and the small vial with C\textsubscript{18}DMS and form a closed system (see Figure 5-13). The oven temperature was kept at 120 °C for another 2 hours. In this manner, the oxide surface was exposed to vapor phase of C\textsubscript{18}DMS for 2 hours, during which the C\textsubscript{18}DMS reacted with the plasma cleaned oxidized wafer surface to form a monolayer on the surface. Afterward, the whole glass system was taken out of the oven, cooled to room temperature (by sitting on the counter), and rinsed (starting here, all the rinsing in this chapter was done by spraying the solvent on the surface) successively with methanol, acetone, ethanol, and water for 5 seconds each. Finally, the surface was dried by a stream of filtered air. The silanized wafer was
finally cut into pieces (1cm x 1cm), rinsed again with water and dried by a stream of filtered air. The silanized wafer was stored in a plastic petri dish sealed by Parafilm to keep it clean prior to use.

**Figure 5-13**: Illustration of the experimental setup for the modification of oxidized Si wafer surface with C_{18}DMS

### 5.3.4 Alignment of λ-DNA

Before use, the silanized wafer (silanized by C_{18}DMS or C_{8}DMS) was heated to 120 °C in an oven for 10 min to remove water molecules attached to the surface and allowed to cool down in air (about 10 to 15 min) prior to use. Afterward, 10 µL of diluted λ-DNA (diluted by 10 times in TE buffer; final DNA concentration was ~65 ng/µL) was transferred onto the silanized surface using a micropipette. DNA solution formed a sphere on the hydrophobic surface. The DNA solution was aligned on the surface by using a Kimwipe paper to absorb and move the solution along one direction. The surface was then dried with a stream of filtered air and was ready for seeding [80].
5.3.5 Ag Seeding of λ-DNA

After alignment of λ-DNA on the silanized surface, 40 µL of a basic silver nitrate solution (0.1M AgNO₃, 0.33 M ammonia hydroxide) was put on the surface using a micropipette and allowed to interact with the DNA for 5 min. Subsequently, the solution on the surface was blown dry along one direction with a stream of filtered, dry air. Then, 40 µL of 0.05M hydroquinone solution was put on the surface to reduce silver ions to metallic Ag nanoparticles. The reaction was allowed to take place for 2 min. The surface was then rinsed with water for 5 seconds and dried with a stream of filtered air. The whole seeding process was performed twice in order to provide an adequate seed density on the λ-DNA.

5.3.6 Electroless Plating

The seeded sample was put into a plastic petri dish and left uncovered. The electroless Ni plating solution consisted of 30g/L NiCl₂·6H₂O, either 0.7 or 2.1 g/L NaBH₄, 60g/L NH₂(CH₂)₂NH₂, 40g/L NaOH, pH=13. Immediately after the preparation of electroless Ni plating solution, 50 µL of this Ni plating solution was transferred onto the sample surface using a micropipette. The petri dish with the sample (with Ni plating solution already on the surface) was immediately put into the water bath with the petri dish floated on the water at either 82°C or 70°C. The electroless Ni plating was allowed to proceed for 1-4 min. After plating, the sample was taken out of water bath, rinsed with water for 5 sec, and dried in a stream of filtered air. Electroless Cu plating solution was prepared and used in a similar way. The electroless Cu plating solution consisted of 5 g/L CuSO₄·5H₂O, 25 g/L KNaC₄H₄O₆ ·4H₂O, 7 g/L NaOH, 10 g/L 37% HCHO, T=65 °C. The plating time was 1-3min for this Cu plating.
5.3.7 Galvanic Displacement Reaction

The 0.01M HTeO$_2^+$ solution for the galvanic displacement reaction was prepared by dissolving 24 mg of TeO$_2$ into 1 mL of concentrated nitric acid overnight (no volume change observed in the dissolution process) followed by dilution with 14 mL of water. Solid bismuth nitrate was added to HTeO$_2^+$ solution to yield a Bi$^{3+}$ concentration of 0.006M, 0.008M, and 0.01M. For the displacement reaction, the sample of DNA-templated Ni or Cu nanowires was put into a humid chamber in order to prevent the solution from evaporating over the extended duration of the process. Then, 60 µL of displacement solution was transferred onto the nanowire surface by using a micropipette. The solution didn’t spread much on the hydrophobic surface. This displacement reaction was allowed to proceed for 2 hours. Then, the surface was rinsed with water for 5 sec and dried in a stream of filtered air.

5.3.8 Conductivity Measurement

After fabrication of the Ni nanowires on a Si surface with 500 nm of thermal SiO$_2$, electron beam lithography, electron beam evaporation, and liftoff were used to make 5 nm Cr / 100 nm Au electrodes. Two-point conductivity measurements were taken at room temperature using a source-drain voltage sweep of +/- 300 mV. National Instruments LabVIEW software was used with Vera Sazonova’s MeaSureit 2.2 VI to perform the measurement.

5.3.9 SEM Imaging

SEM images were taken in the high-vacuum mode on a Philips XL30 ESEM FEG. EDX analysis was also performed on this ESEM using spot scanning with the spot size 6.
5.3.10 AFM Imaging

The samples were imaged in air using tapping mode on a Digital Instruments Nanoscope IIIa MultiMode AFM (Veeco) with silicon AFM tips (AppNano FORTA tips from Nanoscience Instruments, Inc.).
6 CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

To conclude, metallization of branched, open-structured DNA origami with good selectivity has been demonstrated. DNA origami has the potential to provide the increasingly complex templates needed for nanocircuit fabrication. However, these structures also present several challenges for metallization as identified. These challenges include: 1) the stability of the origami in the processes used for metallization, 2) the enhanced selectivity required to metallize small origami structures, 3) the increased difficulty of adhering small structures to the surface so that they will not be removed when subject to multiple metallization steps, and 4) the influence of excess staple strands present with the origami. All of these challenges were addressed in Chapter 3. To be able to metallize the small DNA origami with good selectivity, glutaraldehyde was used to chemically modify DNA and localize Ag seeds only to the DNA templates in solution. DNA origami deposited on the mica surface was rinsed with 4mM MgCl$_2$ or MgAc$_2$, instead of pure water, to keep DNA origami from unfolding. To maintain the structure of DNA during the overnight-dialysis, the staple-to-scaffold ratio was increased from 10:1 to 100:1. The presence of excess staple strands in solution had a significant impact on selectivity. To obtain better selectivity and maintain the origami structure, the staple to scaffold ratio was kept at 10:1 but the concentration of DNA origami was increased from 2 nM to 10 nM. Magnesium addition (MgAc$_2$, 10 mM) to the seeded DNA origami solution was used to promote adhesion of the
seeded origami to the mica surface. Another challenge, the absence of origami on the surface after the plating, was solved by adding MgCl$_2$ to the electroless Au plating solution to yield a final Mg$^{2+}$ concentration of 2 mM. Finally, metallization of DNA origami with good selectivity was achieved. This is the first demonstration of successful metallization of branched DNA origami with good selectivity, which represents important progress towards the realization of DNA-templated nanocircuits.

Following the successful metallization of complete, branched, T-shaped DNA origami, I also demonstrated the site-specific metallization of branched DNA origami in Chapter 4. The site-specific seeding was achieved by modifying staple strands at predesigned locations with binding sites (single-stranded DNA) for the attachment of thiolated DNA coated Au nanoparticles through base pairing. Using this method, T-shaped DNA origami was seeded successfully along one top branch in solution. However, seeding of both top branches of T-shaped DNA origami presented a challenge as identified. The two top branches to be seeded appeared as only one seeded branch after seeding in solution. This challenge was addressed by adsorbing DNA origami to a mica or SiO$_2$ surface so that the branches of DNA origami would not move around during the seeding. Seeded on a SiO$_2$ surface, the average spacing between adjacent Au NPs on origami was 5.8 nm (the median spacing was 4.2 nm) in my work, significantly smaller than that (~15 nm) reported by Pais et al. [77] in a work parallel with that presented here. Then, electroless Au plating was performed on the seeded origami to form continuous nanowires on the seeded area. The smaller spacing in my work led to continuous Au nanowires with an average width of 33 nm after electroless Au plating on a SiO$_2$ surface, smaller than the 50 nm width reported recently by Pais et al. [77]. The relatively uniform Au plating was achieved by a combined use of a modified commercial Au plating solution and Natan’s Au
plating solution. The smallest nanowires prepared here had a width of 20 nm. This is the first time that continuous Au nanowires were prepared on predesigned locations on DNA origami. The continuity of nanowires was verified by conductivity tests—only tests of this nature of which I am aware. Metallization of a template for electronic circuits was one of the ultimate goals for DNA metallization in this research. In this study, I also successfully metallized circuit-shaped DNA origami at predesigned sites, leaving gaps for the localization and operation of semiconductors.

After successful metallization of the complete and specific sites of branched, open-structured DNA origami with Au, I moved forward and demonstrated that we can deposit a variety of materials onto DNA templates selectively to form conductive DNA-templated nanowires for DNA-based nanofabrication. An efficient method to fabricate uniform and conductive DNA-templated Ni nanowires was developed in this work. To accomplish this, it was necessary to adjust the composition of the electroless Ni plating bath to permit deposition at milder conditions in order to be able to keep and plate Ag-seeded DNA on a silanized SiO₂ surface. Conductivity tests showed that these DNA-templated Ni nanowires were conductive. This is the first time of which I am aware that conductive nanowires of a non-noble metal have been fabricated on a DNA template. The resistivity of these DNA-templated Ni nanowires was 3 orders of magnitude higher than that of bulk Ni, comparable to the difference in resistivity observed between the bulk resistivity and the nanowire resistivity for DNA-templated noble metals (Ag, Au, and Pd) [36, 37, 52, 54, 56, 67, 70, 71, 81]. Additionally, a new method was developed for the fabrication of DNA-templated Cu nanowires. These Cu nanowires were fabricated using Ag seeding and electroless Cu plating, and may be useful for the fabrication of DNA-templated nanoelectronic circuits. In addition, I have successfully demonstrated a galvanic
displacement method for the fabrication of DNA-templated semiconductor nanowires. The galvanic displacement method provides the opportunity to deposit a variety of materials that haven’t been (or couldn’t be) deposited onto DNA through other methods. Using this galvanic displacement method, continuous DNA-templated Te and Bi$_2$Te$_3$ nanowires have been fabricated in simple processes. Among other things, these Te and Bi$_2$Te$_3$ nanowires may be useful for thermoelectrical applications. In addition, it may be possible to use the galvanic displacement method demonstrated here to make DNA-templated nanowires of a variety of other semiconductors and metals such as Ge, Ag, Au, Pt, and Pd with good selectivity. Altogether, these results represent important progress toward the realization of DNA-templated nanofabrication.

6.2 Future work

There are many opportunities for future work related to this research. These opportunities include: 1) controlling the seeding and plating to get smaller metal nanowires at predesigned locations on DNA origami for DNA-templated nanoelectronic circuits, 2) testing and adjusting the physical properties of DNA-templated Te and Bi$_2$Te$_3$ nanowires, 3) depositing semiconductor materials onto predesigned locations on DNA origami template for nanoelectronic circuits, 4) attaching Au NPs site-specifically to DNA origami and enlarging the Au NPs for applications in plasmonics, and 5) building systems such as sensors and circuits using the processes developed in this research.

First, the seeding and plating can be controlled to get smaller metal nanowires at predesigned locations on DNA origami for DNA-templated nanoelectronic circuits. If the seeding process used in this study can be further improved such that the maximum spacing between neighboring Au NPs is not greater than 4.2 nm (currently our median spacing), and the
plating solution can plate uniformly, continuous nanowires with a width of 12 nm may be prepared on pre-designed locations on DNA origami. The large spaces between Au NPs on DNA origami could be reduced by filling with Au NPs if a higher concentration of Au NPs or a significantly longer time (i.e. 24 hrs, instead of 30 min) is used for the seeding. Plating additives may also be helpful in increasing the uniformity of the electroless plating [42].

Second, the physical properties of DNA-templated Te and Bi$_2$Te$_3$ nanowires can be tested and adjusted. The physical properties such as thermal and electrical conductivities, and thermoelectric properties of Te and Bi$_2$Te$_3$ nanowires can be tested. The physical properties of Te and Bi$_2$Te$_3$ nanowires can be adjusted by adjusting the composition of the material and perhaps introducing specific impurities (dopants) into these nanowires. Also, as demonstrated in this research, the diameter of these nanowires can be adjusted using different methods. This provides additional methods to adjust the physical properties of DNA-templated Te and Bi$_2$Te$_3$ nanowires.

Third, semiconductor materials can be deposited on pre-designed locations on DNA origami templates and assembled with metal nanowires to form complete nanoelectronic circuits. For instance, semiconducting carbon nanotubes could be located onto pre-designed locations on a DNA origami template [145]. Then, the process developed in Chapter 4 can be used to form continuous nanowires on the designated sites on DNA origami and form a complete circuit with the carbon nanotubes.

Fourth, Au NPs can be deposited site-specifically onto DNA origami and enlarged for applications in plasmonics. To construct plasmonic structures, the size and the arrangement of nanoparticles are of great importance. DNA origami can be used to assemble Au nanoparticles in a variety of patterns, as shown in this research. Electroless plating can be used to enlarge the Au
NPs to the desired size by controlling the plating time. The use of additives in the plating solution to slow down the plating could help control the size of the plated particles effectively and precisely. AFM can be used to measure the height of the structures formed on DNA origami templates. SEM and TEM can also be used to characterize the size and morphology of the structures. EDX can be used to characterize composition. Fourier transform infrared spectroscopy and fluorescence spectroscopy can be used to characterize the optical properties of the structures assembled on the surface.

Fifth, it should be possible to build systems such as sensors using the processes developed in this research. For instance, nanowires can meet the demands of next-generation sensors that require significant improvements in sensitivity, specificity and parallelism [103]. DNA origami provides the possibility of constructing the template for such sensor systems. The metal deposition techniques and the galvanic displacement processes developed here can be used to fabricate nanowires of a variety of materials needed for sensors to detect diverse analytes, such as glucose and DNA [103].

Thus, the precise control of the deposition of materials into different patterns and the ability to control the size of these metallic and semiconductor materials, as developed in this work, should enable the fabrication of nanodevices in different fields in the future. I believe that DNA-templated nanofabrication will have a bright future.
REFERENCES


