DIP-PEN NANOLITHOGRAPHY OF ELECTRICAL CONTACTS TO ORGANIC NANOSTRUCTURES

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Abstract

The continuous drive towards nanoelectronics prompts development of alternative semiconductors that are compatible with silicon technology platforms and provide higher carrier mobilities than silicon. Since carbon nanotubes and their planar counterpart, graphene, are characterized by intrinsic carrier mobilities orders of magnitude higher than Si with near-ballistic transport, they hold promising potential for next-generation nanoelectronics. While graphene and carbon nanotubes are potential extensions of silicon-based nanoelectronics, pi-conjugated hydrocarbons may enable circuitry on substrates other than silicon. These solution-processable organic field-effect transistors can be manufactured on flexible, conformable, and stretchable plastic substrates, filling a niche range of applications operating at relatively low-frequencies, such as flexible displays and chemical sensors.

Engineering of these organic-based devices requires further fundamental studies on the material charge transport properties and their dependence on device configuration to develop structure/property relationships and an understanding of device physics. The goal of these fundamental studies is to enable the rational synthesis of functionality-specific materials and design of high-performance devices. However, correlating the intrinsic charge transport properties of organic semiconductors to their structural order remains a challenge, partly due to the difficult fabrication of the nanoscale devices required for such studies, e.g., 1D isolated carbon nanotubes, 2D graphene sheets, and 3D single crystals or grains of pi-conjugated molecules. Conventional methods of producing single carbon nanotube and graphene
devices have used electron-beam lithography (EBL), whereas the intrinsic properties of hydrocarbon-based organic semiconductors have been studied mainly through manual patterning of single crystals.

This thesis focuses on developing dip-pen nanolithography (DPN) as a method for fabricating such nanoscale devices to facilitate these fundamental studies. DPN is a scanning probe-based technique that combines the nanoscale resolution of EBL with the direct writing of microcontact printing. In DPN a scanning probe tip is coated with a molecular ink and acts as a nanoscale quill to directly pattern this ink on substrates, thereby forming functional nanostructures. The potential advantages of using DPN as a nanoscale patterning alternative to EBL include mild processing conditions (lack of electron beam irradiation) and ease of use and accessibility of AFM systems.

Two schemes for DPN-patterning of electrical contacts were explored: 1) a direct patterning method in which DPN was used to deposit Au nanoparticles (NPs) that would eventually be chemically grown into conductive leads, and 2) an indirect patterning method in which DPN was used to deposit an alkanethiol on Au, acting as a mask against subsequent Au etching to reveal electrical contacts.

In the first scheme, a procedure was developed for increasing the loading of Au nanoparticles onto AFM tips to prolong patterning life. AFM tips were subsequently imaged by scanning electron microscopy to determine ink coverage and gain insight into the deposition process. The Au NPs have a diffusion profile consistent with the Stokes–Einstein equation and, unlike other molecular DPN inks, Au NPs do not diffuse laterally on the substrate surface during deposition. Next, surface interactions, relative humidity and writing speed were controlled to determine an optimal range of
conditions for deposition. Various ink-substrate combinations were studied to elucidate the dependence of deposition on interactions between Au nanoparticles and the substrate surface.

Results indicate that a highly hydrophilic surface is required for Au nanoparticle deposition, unless covalent binding can occur between the Au and substrate surface. The optimal range of relative humidity for patterning was found to be 40% to 60%, and Au nanoparticle deposition was not sensitive to writing speeds ranging from 0.01 \( \mu \text{m/s} \) to 2 \( \mu \text{m/s} \). Experiments with different ink-solvent systems were conducted in an attempt to promote more homogeneous patterns; however, our preliminary results indicate that more optimization of this variable is necessary. Various issues such as pattern inhomogeneity and limited electroless development of the Au NP patterns render this direct Au NP patterning method unsuitable for making electrical contacts and led us to pursue the second scheme for DPN patterning.

In this indirect patterning scheme, proof-of-concept was demonstrated by creating single-walled carbon nanotube (SWNT) devices. Electrical contacts to individual and small bundle single-walled carbon nanotubes were masked by an alkanethiol that was deposited via DPN on a thin film of Au evaporated onto spin-cast, non-percolating, and highly isolated single-walled carbon nanotubes. A wet Au etching step was used to form the individual devices. The electrical contacts were comparable in conductivity to those made with EBL. Furthermore, the electrical characteristics for three different single-walled carbon nanotube devices – semi-metallic, semiconducting and metallic – were analyzed and indicated performance consistent with literature reports for isolated, solution-processed single-walled carbon nanotube devices.
fabricated *via* EBL. Raman analysis on representative devices corroborates the results from AFM imaging and electrical testing.

These optimized fabrication conditions were then applied toward making electrical contacts to monolayer graphene. The slightly higher resistivity values of DPN-generated graphene devices versus those fabricated *via* EBL led us to investigate possible damage to the graphene from processing. Indeed, damage was inflicted on the graphene flakes during Au deposition and subsequent etching and a nanoparticle residue remained on the graphene after processing. Therefore, DPN did not perform better than EBL for making contact to graphene, mainly due to fracture during Au deposition and etching to define monolayer graphene structures.

Finally, preliminary experiments were conducted on DPN masking of electrical contacts to organic semiconducting grains. However, direct deposition on Au onto these monolayer grains is not a viable method due to penetration of Au through the thin organic layer. Alternative fabrication schemes based on Au film transfer and subsequent DPN masking are discussed. Modification of the developed DPN method may facilitate fundamental studies on the electrical properties of these nanostructures that are not amenable to the processing conditions used in EBL.
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1. Introduction

This chapter provides background for and discusses the motivation and goals of dip-pen nanolithography of electrical contacts to organic nanostructures. Section 1.1 addresses the purpose of studying organic nanostructures for electronic applications. The potential of dip-pen nanolithography (DPN) as a method for fabricating organic nanoelectronic devices is assessed in Section 1.2. Next, Section 1.3 discusses the overall design and objectives in applying DPN towards patterning electrical contacts. Finally, the organization of this thesis is outlined in Section 1.4.

1.1. Motivation for Organic Nanoelectronics

As a result of the continuous lateral and vertical scaling down of silicon FETs, particularly the reduction of gate dielectric thickness to below 2 nm, charge leakage due to quantum mechanical tunneling increases to more than 1 A/cm² [1], causing problems related to off-state current, power consumption, and heat dissipation. Replacing the thermally grown SiO₂ with a deposited metal oxide that has a larger permittivity, such as HfO₂, can reduce the leakage current. However, it is more difficult to control the interface quality and scattering with a deposited dielectric, causing a decrease in carrier mobilities to about 200 cm²/V/s for electrons and 40 cm²/V/s for holes [2]. Therefore, alternative semiconductors that are compatible with nanoscale silicon technology platforms and that provide higher carrier mobilities than silicon are of great interest. Since graphene and its tubular counterpart, carbon nanotubes, are characterized by intrinsic carrier mobilities several orders of magnitude
higher than Si with near-ballistic transport, these materials have much potential for
next-generation nanoelectronics.

Graphene is a single layer of graphite – carbon atoms densely packed into a
benzene-ring structure (Figure 1.1a). This 2D material is a zero-band gap
semiconductor, i.e., graphene conducts charge like a metal but exhibits an ambipolar
electric field effect [3]. However, when graphene is patterned into narrow nanoribbons,
the carriers are confined to a quasi-1D system, thereby opening a band gap that scales
inversely with the ribbon width. Therefore, it is possible to engineer the energy gap of
graphene nanostructures for semiconducting applications [4]. Besides being of interest
for fundamental studies of quantum relativistic phenomena [5], graphene has been
applied in field-effect transistors [6, 7], chemical sensors [8, 9], and as an electron-

If graphene nanoribbons are rolled into cylinders, they become carbon nanotubes –
1D systems typically of nanometer diameter and microns in length (Figure 1.1b).
Their chirality determines their band gap and hence electrical properties: zero-gap
(metallic), small-gap (semi-metallic), and large-gap (semiconducting) [14]. Single-
wall carbon nanotubes (SWNTs) have demonstrated their unique electrical
properties as components in single-electron [15] and field-effect transistors [16-18],
chemical sensors [19-21], and transparent electronics [22-24]. Engineering these
carbon nanotube-based devices requires further fundamental studies on SWNT charge
transport properties [25, 26] and their dependence on device configuration [27].
While graphene and carbon nanotubes are potential extensions of silicon-based nanoelectronics, thin films of pi-conjugated hydrocarbons and the zero-dimensional fullerenes, (Figure 1.1c) may enable organic field-effect transistors (OFETs) and integrated circuits on substrates other than silicon. An OFET is a three-terminal device constructed with the following basic components: electrodes (gate, drain, and source), a dielectric layer, and a semiconducting layer (Figure 1.1d).

Since all the functional materials required to fabricate solution-processable OFETs can be deposited and patterned at or near room temperature, these devices can be manufactured on flexible, conformable, and stretchable plastic substrates. These characteristics allow OFETs to fill a niche range of applications, such as flexible displays and artificial skin for sensing pressure, chemical contaminants, and other environmental variables. Since these applications require large-area distribution of circuits that can operate at low-frequencies, the carrier mobilities of organic semiconductor (OSC) films (~1 cm²/Vs) are usually sufficient [28]. OFETs have already been incorporated into electronic paper [29], flexible displays [30], sensors
Currently, charge transport in these materials is usually measured via thin-film transistors, which are limited by variations in overall molecular order and device quality. The charge carriers can be trapped by grain boundaries and defects present in these thin-film transistors. Characterization of the intrinsic OSC physical properties is necessary for developing structure/property relationships that could enable the rational synthesis and design of new high-performance and functionality-specific materials. Furthermore, as OFETs approach the nanoscale, device physics become more complex and contact resistance plays a larger role in defining device performance. Therefore, characterization of these effects and the fundamental properties of materials at the nanoscale via model systems is necessary for engineering their performance.

Predictable and controllable nanostructure growth enables the assembly of materials with distinct chemical composition, structure, size and morphology for specific functional devices and integrated circuits [33]. This 'bottom-up' approach to device fabrication may be a solution to the technological challenges faced by the semiconductor industry and could lead to new strategies for increasing overall device density through scaling in three dimensions.

1.2. **Motivation for Dip-Pen Nanolithography**

This thesis focuses on developing DPN as a method for fabricating these nanoscale devices to facilitate the important fundamental studies discussed in the previous section. Conventional methods of producing single carbon nanotube and graphene devices have used electron-beam lithography (EBL), whereas the intrinsic properties of
nanostructured OSCs have been studied mainly through manual patterning of single crystals. The potential advantages of using DPN over these methods, in particular as a nanoscale patterning alternative to EBL, are discussed in the respective chapters focusing on SWNT (Section 3), graphene (Section 4), and OSC (Section 5) device fabrication. In brief, the mild processing conditions (lack of electron beam irradiation) and ease of use and accessibility of AFM systems (as compared to EBL) are major advantages of the DPN approach towards nanostructure fabrication.

DPN is a scanning probe-based technique that combines the nanoscale resolution of EBL with the direct writing of microcontact printing [34]. In DPN, an AFM probe is used as a carrier and nanoscale delivery system for the direct constructive patterning of various inks on surfaces to form functional nanostructures (Figure 1.2). In this method, the ink coating the AFM tip is transported upon contact of the scanning tip with the surface through a meniscus of condensed water vapor that forms between the tip and the surface. DPN was first demonstrated with alkanethiol molecules [35], which could be delivered to a Au surface with 15 nm resolution, and the deposited structures were stable, crystalline and indistinguishable from self-assembled monolayers (SAMs) grown in bulk solutions [36]. The ensuant research explored the versatility of DPN with a wide range of substrates and inks such as silanes [37, 38], polyelectrolytes [39, 40], conducting polymers [41-43] and biological molecules [44-46] (Figure 1.2). Currently, sub-50-nm resolution in the patterning of surfaces has been achieved [47].
1.2.1. DPN Mechanism

Although the experimental procedure for DPN is relatively simple, the underlying physical mechanism is quite complicated and still partially under debate. This is due to the large number of parameters that can influence ink transport from the tip to the substrate. Such factors include the chemical nature of all the components (tip, substrate, ink, solvent), humidity, temperature, tip shape and contact area, as well as the instrumental parameters chosen for writing (scan speed, dwell time, contact force).

There is a general consensus, however, that ink transport can be divided into several steps. The first involves the formation of a meniscus (typically water unless a special saturated solvent setup is used) between the tip and the substrate, providing a bridge for the ink transport. Theoretical studies have predicted an increase in the size of the meniscus with increasing humidity and decreasing tip-sample separation [48]. Furthermore, experimental confirmation of the presence of such a meniscus has been obtained by environmental scanning electron microscopy [49].
The second step is the detachment of the ink from the tip and the subsequent transfer to the sample surface, determining the deposition rate. This step is strongly influenced by the meniscus and the environmental conditions in general, as shown with 16-mercaptohexadecanoic acid (MHA) [50]. An increase in the deposition rate is observed with an increase in temperature due to an enhanced dissociation of the molecules from the cantilever and a higher solubility in the water of the meniscus.

Another effect influencing the ink transfer is the shape and size of the meniscus as a function of the substrate surface hydrophilicity. If the surface is hydrophobic, then the contact area of the water meniscus is smaller, limiting the effective area upon which ink transport can occur. In the case of a hydrophilic surface the meniscus can spread out, increasing the ink flux toward the substrate [51].

Since the dimensions of the meniscus play a crucial role in DPN, changes in the humidity are also expected to influence the ink transfer. For MHA an increase in the deposition rate is observed with increasing humidity. However, the rate for octadecanethiol (ODT) is nearly unchanged and may even decrease slightly with increased humidity [52]; this opposite effect is attributed to the hydrophobic nature of ODT.

It should also be noted that the transfer rate is not constant over the course of an experiment, even if the environmental parameters are constant. Rather, the deposition rate depends on the tip-substrate dwell time (due to different diffusion regimes) [53] and on the number of depositions performed with a single tip (due to depletion of material) [54]. The AFM tip has been modeled both as a source of constant ink flux in terms of two-dimensional diffusion [55] and as a source of constant ink concentration
The latter results yield an expression for the surface ink concentration as a function of both deposition time and distance from the AFM tip, and these calculations match experimental data slightly better than the former model over the range of contact times studied. However, neither model has been tested systematically over a large range (several orders of magnitude) of contact times. Such an experiment would more clearly identify the assumptions behind the tip serving as a source of constant flux or constant concentration. It is possible that under different patterning conditions the tip may be more accurately modeled by a particular assumption.

After ink dissociation from the tip and diffusion through the water meniscus, the final step in the DPN process is the diffusion of the species on the substrate surface. Therefore, there seem to be two transport regimes: one for short contact times/high scan speeds in which the kinetics of ink detachment from the tip dominate and another for long contact times/slow scan speeds during which ink diffusion limits the pattern growth kinetics [57]. This latter regime is heavily influenced by the number and strength of the binding sites on the substrate surface. For a large number of strong binding sites, as is the case for thiols on gold, the molecules that are in contact cannot undergo rearrangement. Thus, the surface diffusion occurs through a second layer of molecules on top of the immobilized self-assembled monolayer (SAM) [58]. When the binding is weaker, the bound molecules can undergo rearrangement, resulting in a loss of pattern fidelity [59].

Therefore, the ideal ink-substrate system for DPN can be characterized with an ink that has low activation energy for dissociation from the AFM tip (yet still coats the tip uniformly and with enough density to ensure a constant and high concentration
gradient), high solubility in water so as to enhance diffusion through the meniscus, and a chemical affinity for the substrate surface so as to retain pattern fidelity.

1.3. Thesis Project Objectives

The goal of this thesis was to develop and evaluate DPN for patterning electrical contacts to organic nanostructure devices (1D SWNTs, 2D graphene and 3D OSCs). To this end, two fabrication schemes were explored (Figure 1.3): 1) a direct patterning method in which DPN was used to deposit Au nanoparticles (NPs) that would eventually be chemically grown into conductive leads, and 2) an indirect patterning method in which DPN was used to deposit an alkanethiol on Au, acting as a mask against subsequent Au etching to reveal electrical contacts. Although DPN of 16-mercaptohexadecanoic acid has been used to generate a resist layer on Au films for patterning Au nanostructures on silicon [60], thereby characterizing the DPN step in Scheme 2, this subtractive approach requires extra steps in coating the substrate surface with a thin film of Au and etching exposed Au. Therefore, the direct approach in Scheme 1 is preferable if it is versatile in application to various substrates. Since DPN of Au NPs has not been well characterized in the literature, the first part of this thesis focused on exploring the parameter space for DPN of Au NPs on substrates in general and not just on organic nanostructures. Issues encountered at both stages of Scheme 1 (DPN of Au NPs and their growth into conductive electrodes) prompted us to consider an alternative route towards our goal, hence the indirect patterning method illustrated in Scheme 2.
Once proof-of-concept for DPN of electrical contacts via Scheme 2 was shown for SWNTs, modifications to this method were developed to fabricate contacts to graphene flakes and OSC grains. Of equal importance to the actual demonstration of functional devices was the characterization of the DPN processing effects on these organic nanostructures to determine whether any damage was incurred that would detract from using DPN as a method for generating electrical contacts.

1.4. Outline of Thesis

Chapter 2 discusses the direct writing of Au NPs on various substrates and characterizes the conditions for optimal deposition. The indirect patterning of
electrical contacts is demonstrated for single-walled carbon nanotubes and graphene in Chapters 3 and 4, respectively. Finally, preliminary results in translating this DPN-patterning technique to OSC grains are presented in Chapter 5. Overall conclusions from this body of work are discussed in Chapter 6, and references are provided in Section 7.
2. Direct Patterning of Gold Nanoparticles

Various methods for the patterned assembly of metal nanoparticles have been developed in order to harness their unique electrical and optical properties for device applications. This chapter discusses a method for direct writing of gold nanoparticles (Au NPs) at nanoscale resolution using dip-pen nanolithography. A brief literature review of Au NP patterning is presented in Section 2.1. The experimental design of this study and the materials and methods used are discussed in Sections 2.2 and 2.3, respectively. The results of this study are presented in Section 2.4 and are summarized in the next paragraph.

A procedure was developed for increasing the loading of Au nanoparticles onto AFM tips to prolong patterning life (Section 2.4.1). AFM tips were subsequently imaged by scanning electron microscopy to determine ink coverage and gain insight into the deposition process. Next, surface interactions, relative humidity and writing speed were controlled to determine an optimal range of conditions for deposition (Sections 2.4.2-2.4.4). Various ink-substrate combinations were studied to elucidate the dependence of deposition on interactions between Au nanoparticles and the substrate surface; inks consisted of positively and negatively-charged particles and substrates were SiO$_2$ surfaces modified as hydrophilic or hydrophobic and interacted electrostatically or covalently with Au nanoparticles.

Results indicate that a highly hydrophilic surface is required for Au nanoparticle deposition, unless covalent binding can occur between the Au and substrate surface. The optimal range of relative humidity for patterning was found to be 40% to 60%, and Au nanoparticle deposition was not sensitive to writing speeds ranging from 0.01
μm/s to 2 μm/s. Experiments with different ink-solvent systems were conducted in an attempt to promote more homogeneous patterns (Section 2.4.5); however, our preliminary results indicate that more optimization of this variable is necessary.

Sections 2.5 and 2.6 discuss the various issues such as pattern inhomogeneity and limited electroless development of the Au NP patterns render this direct Au NP patterning method unsuitable for making electrical contacts. Alternatives such as direct reduction of Au and DPN of a liquid silver ink are discussed in Section 2.7 and 2.8, respectively. Conclusions of this study are presented in Section 2.9.

The results of this study were published in *ACS Nano* [61]. Wechung Maria Wang wrote the paper and performed all the research and data analysis, except for the following: SEM and TEM data were taken by Shuhong Liu, and AES data were taken by Randy Stoltenberg.

### 2.1. Background

The patterned assembly of Au nanostructures has garnered much interest due to their unique electrical and optical properties [62], which have led to several applications in electronics [63-65], chemical [66] and biological [67] sensing, catalysis [68] and optics [69]. To achieve precise ordering of these materials for devices, various patterning techniques such as electron-beam lithography and microcontact printing have been developed [70]. More recently, dip-pen nanolithography (DPN) has emerged as a scanning probe-based technique that combines the nanoscale resolution of EBL with the direct writing of microcontact printing [34].
Although DPN has been used for the direct write of Au NPs [71-73], results in the literature conflict or are incomplete regarding the importance of various factors such as contact force and substrate effects. For instance, Thomas et al. reported that pattern dimensions were independent of the applied contact force whereas Ben Ali et al. observed strong contact force dependence. Furthermore, Garno et al. used a covalent linkage between the Au NPs and the substrate surface to limit lateral diffusion of patterns; however, the need for such specific interactions has not been proven. Moreover, the extent of patterning was limited in all studies due to low throughput presumably caused by depletion of ink (Figure 2.1).

![AFM topograph and cursor profile](image)

**Figure 2.1.** (A) AFM topograph (550 × 550 nm²) of a decanethiol SAM, where a 150 × 450 nm² rectangle of thiol-modified gold nanoparticles were placed with nanometer precision. (B) Corresponding cursor profile for (A). Reproduced from Ref. [72]. Copyright 2003 American Chemical Society.

For continuous feeding of ink, a microfluidic nanofountain probe was developed with an annular aperture and an ink reservoir. This probe was used to pattern arrays of Au NPs – resulting in dots as small as 200 nm in diameter [74] and lines as thin as 100 nm [75]. However, the resolution of these printed features was ultimately limited by the aperture of the nanofountain probe, which was fabricated via a multi-step micromachining process. Other attempts at using a scanning probe tip for patterning
Au nanostructures have involved application of electric fields [76-78], surface reduction of Au salt [79] and biocatalysis [80].

2.2. Experimental Design

We have developed a facile method using commercially-available AFM tips for high-resolution, direct patterning of Au NPs on a variety of surfaces and length scales (individual particles to clusters and nano- to micrometer patterns). Based on previous ink-substrate studies, we expected that various parameters would influence ink transport: chemical composition of the ink and substrate surface, AFM tip shape and surface chemistry, distribution and mobility of ink on the tip, and environmental conditions (temperature and humidity) of the experiments [57].

This study investigated five variables in the deposition process: ink loading, surface interactions (ink-substrate and ink-AFM tip), relative humidity (RH), writing speed and ink-solvent system. First, a procedure was developed for increasing the loading of Au NPs onto AFM tips to prolong patterning life. Since ink transport is thought to occur via the water meniscus that forms between the AFM tip and the substrate [50], the Au NPs used in this study were water soluble. Deposition of Au NPs occurs when their affinity for the substrate overcomes that for the tip and any cohesive forces within the ink itself. To promote transfer of ink to the substrate, the Au NPs were dispersed in either water or methanol, both low viscosity solvents, and then weakly physisorbed on the tip via an additive inking process. Next, various ink-substrate combinations were studied to elucidate the dependence of deposition on interactions between Au NPs and the substrate surface; inks consisted of positively
and negatively-charged Au NPs and substrates were similarly or oppositely charged, hydrophilic or hydrophobic, or capable of binding to Au via a thiol functionality. Furthermore, ink-AFM tip interactions were studied by chemically modifying the surfaces of AFM tips. Next, RH and writing speed were varied to determine an optimal range of conditions for deposition. Other DPN inks such as alkanethiols have well-characterized behavior under a range of RH and writing speed [53]; however, to our knowledge, no such study has been reported for Au NPs. Finally, mixed solvent systems were formulated to impart more fluid-like properties to the Au NP ink.

2.3. Materials and Methods

2.3.1. Gold Nanoparticles

The base inks used in this study consisted of aqueous solutions of negatively-charged citrate-capped Au NPs (C-Au NPs, 5 nm nominal diameter; Sigma-Aldrich), aqueous solutions of positively-charged amine-capped Au NPs (Nanogold, 1.4 nm; Nanoprobes, Inc.) and methanolic solutions of positively-charged 4-\((N,N\text{-dimethylamino})\) pyridine-capped Au NPs (DMAP-Au NPs, average diameter 5 nm). The respective concentrations of C-Au NPs, Nanogold and DMAP-Au NPs were approximately \(5.1 \times 10^{13}\) particles/mL, \(1.8 \times 10^{16}\) particles/mL and \(1.6 \times 10^{15}\) particles/mL. DMAP-Au NPs were synthesized according to a published procedure [81], and particle concentration was determined by UV-Vis spectroscopy (assuming an extinction coefficient of \(10^7\) based on an average particle size of 5 nm [82]). Refer to Figure 2.2 for the corresponding transmission electron microscopy (TEM) image and UV-Vis spectrum.
Briefly, the synthesis of DMAP-Au NPs involved first dissolving 9 mg of AuCl$_3$ by sonication in 3 mL of 100 mM didodecyldimethylammonium bromide (DDAB) in toluene. Next, 0.06 mL of tetrabutyl ammonium hydroxide (37% in methanol) was added, turning the solution from orange to yellow. Finally, 30 mg of tetrabutyl ammonium borohydride dissolved in 1.2 mL DDAB solution was injected to the gold salt solution under stirring and N$_2$ purging. After 3 hours, ligand exchange was performed by precipitating the Au NPs with a few drops of methanol/ethanol and centrifuging for 5 min. at 14000 RPM. The Au NPs were then resuspended in a methanolic solution of 0.1 M DMAP.

2.3.2. Surface Preparation

Silicon wafers with 300-nm thermally-grown oxide layers (Silicon Quest International) were diced into centimeter-sized pieces. Markers were scratched into
the silicon using a diamond scribe to enable registration of imaging tip with Au NP patterns. For relative humidity studies, a silicon substrate with lithographically-patterned markers was obtained from Nanoink, Inc. All substrates were cleaned for at least 20 min. in a UV-ozone cleaner (Model 42, Jelight Company Inc.) before further surface modification and patterning.

Surface treatment with poly-L-lysine (Ted Pella, Inc.) followed previously published protocol [83]. Briefly, SiO$_2$ pieces were exposed to a poly-L-lysine solution (1 ppm in water) for 3-5 minutes and then rinsed with deionized water. SiO$_2$ pieces were functionalized with mercaptopropyltrimethoxy silane through immersion in a 2% v/v solution in ethanol overnight at room temperature. The substrates were then rinsed with and sonicated in ethanol, and cured in an 80 °C oven for 30 min. Amino functionalization of SiO$_2$ occurred through vapor deposition of aminopropyltrimethoxy silane under vacuum overnight. Finally, hydrophobic SiO$_2$ was obtained by vapor deposition of pentafluorophenyl propyl trichlorosilane under vacuum and heating at 80 °C for 30 min. All silanes were obtained from Gelest, Inc.

### 2.3.3. Patterning and Imaging

Patterning (contact mode, setpoint 1.5 to 2 V) and imaging (AC mode) were performed on an NSCRIPTOR DPN system (Nanoink, Inc.) at ambient temperatures (26 °C ± 4 °C) and variable relative humidity set by the environmental chamber (a beaker of boiling water was placed in the chamber to ramp up humidity quickly). Line, dot and boundary patterns were created using InkCAD software, which allowed for the specification of writing speeds and dwell times. Au NPs were inked onto the
diving-board cantilevers of types A and C Si$_3$N$_4$ probes (nominal spring constants 0.041 N/m and 0.061 N/m, respectively) obtained from Nanoink, Inc. Au NP patterns were imaged using Si probes obtained from Nanoink, Inc. and Nanosensors, with nominal force constants of 42 N/m and nominal resonance frequencies of 320-330 kHz. AFM images were flattened using the Scanning Probe Image Processor (SPIP, Image Metrology A/S).

AFM tips were imaged on an FEI XL30 Sirion SEM operated at acceleration voltages ranging from 2 to 5 kV. AES data were taken on a PHI 700 Auger Nanoprobe (Physical Electronics, Inc.).

### 2.4. Optimization of Deposition Conditions

#### 2.4.1. Ink Loading

Limited patterning occurred when the AFM tips were functionalized via the dip-coating method commonly used for DPN inks. The extent of patterning correlated with Au NP concentration; tips dip-coated with Nanogold and DMAP-Au NPs sometimes produced patterns while C-Au NPs, which were of the lowest concentration, could not be patterned. Therefore, we developed an inking method for saturating Au NPs on AFM tips to achieve consistent patterning.

The Au NPs were loaded onto a Si$_3$N$_4$ AFM tip via a micropipetter dispensing 5 µL droplets. To efficiently load the tip, the ink was confined to the cantilever by placing Parafilm under and on top of the probe (Figure 2.3a). The hydrophobic nature of Parafilm ensured that the droplets would stay on the cantilever at a high contact angle rather than spread to the rest of the probe. To concentrate the Au NPs on the tip,
solvent evaporation was accelerated by heating the probe to 60 °C – 70 °C under a saturated water vapor environment. This inking procedure was repeated three to five times for sufficient loading of Au NPs, which was verified using scanning electron microscopy (SEM) in Figure 2.3b. A freshly-coated tip was then used for continuous patterning until depletion of ink from the tip, again verified with SEM (Figure 2.3c). Typically, such inked tips deposited Au NP patterns spanning several microns.
2.4.2. Surface Interactions

2.4.2.1. Ink-Substrate

The base substrate used in this study was silicon with a thermally-grown oxide layer (300 nm). This SiO₂ surface is commonly used for device fabrication, well
characterized and easily functionalized. To promote the formation of a water meniscus between the AFM tip and the substrate, the SiO$_2$ was rendered hydrophilic (static water contact angle $\approx 0^\circ$) by UV-ozone (UVO) treatment.

Since SiO$_2$ was negatively charged under the conditions of our deposition (above pH 3.5) [84], DPN of positively-charged DMAP-Au NPs and Nanogold was attempted with the hypothesis that electrostatic attraction would aid Au NP printing. Both of these Au NPs were successfully patterned via DPN on UVO-treated SiO$_2$ at ambient temperatures and RH above 40%. Conditions such as RH and writing speed will be discussed in later sections.

Figure 2.4a and Figure 2.4c show AFM images of patterned DMAP-Au NPs. The heights of the particles in the line and boundary patterns are 2.5 ± 0.9 nm and 5.1 ± 1.9 nm, respectively. The thermal stability of these patterns was verified by annealing at 165 °C for 30 minutes (Figure 2.4b,d). The heights of the annealed particles were comparable to those before annealing: 3.3 ± 1.1 nm and 5.3 ± 1.3 nm for the line and boundary patterns, respectively.

Based on TEM analysis of DMAP-Au NPs (Figure 2.2), particle size ranges from 1 to 8 nm. Since the lines were patterned before the boundary pattern using the same inked tip, we can conclude that smaller particles deposit first, followed by larger particles and aggregates. This result has also been observed with C-Au NPs (see Section 2.4.4) and is in accordance with the Stokes–Einstein equation, which predicts that smaller particles have a higher diffusivity [85].
The high diffusivity of Nanogold resulted in patterning of aggregates (Figure 2.5a), as opposed to the single-particle deposition observed for DMAP-Au NPs. The valley in the middle of the patterned line in Figure 2.5a is due to Nanogold depositing from the sides of the AFM tip onto the substrate [86]. To verify that the deposited material was indeed composed of Au NPs, the pattern was exposed to an electroless gold development solution (GoldEnhance EM from Nanoprobes, Inc.) for 5 minutes. Subsequent AFM scans revealed that the Au NPs approximately doubled in height (Figure 2.5b).
Figure 2.5. AFM topographic images rendered in 3D of Nanogold patterns on UV-ozone cleaned SiO$_2$ before (a) and after (b) gold development.

DPN of negatively-charged Au NPs on a positively-charged substrate was also demonstrated by using C-Au NPs as the ink and SiO$_2$ treated with poly-L-lysine as the substrate. The resultant patterns of Au NP dots are shown in Figure 2.6. The goal of dot patterning is to deposit a single Au NP in a precise location. Line patterns of C-Au NPs on poly-L-lysine-treated SiO$_2$ are also shown in Section 2.4.4 (Figure 2.14).

To verify that the deposited material was indeed Au, chemical analysis was performed on patterned C-Au NPs via Auger electron spectroscopy (AES). Preliminary AES spectra indicated high carbon content and no Au peak was observed. The carbon signal was likely from citrate ions that comprise the ink matrix to stabilize the Au colloid. Since Auger electrons have a mean escape path of a few nanometers at most, an adequate signal from Au was detected only after eliminating the organic layers via thermal annealing and UVO-cleaning of the patterns. These organic layers were deposited on the tip due to serial concentration during the ink loading step. Figure
2.7a shows an SEM of the Au features and the corresponding AES spectrum, which contains the Au (MNN) transitions at 2018 eV and 2100 eV. The peak for the Au (NVV) transition is not shown because it is convoluted with the low energy peak for SiO₂.

The AES data indicate that the DPN-generated patterns were indeed composed of Au NPs; however, it seems that the organic matrix stabilizing the Au NPs was also deposited. In fact, treatment of patterned DMAP-Au NPs and C-Au NPs with gold development solution (more details in Section 2.6) resulted in significantly less growth than that of patterned Nanogold, which is not suspended with organic stabilizers in solution and hence more of the Au surface is exposed for reaction. Furthermore, AES analysis of AFM tips freshly-inked with C-Au NPs indicates the presence of an organic matrix. The Auger spectrum in Figure 2.7b contains peaks for C (265 eV), O (510 eV) and Na (994 eV), reflecting the composition of trisodium citrate, as well as weaker peaks for Au.
Figure 2.7. (a) Derivatized Auger spectrum of C-Au NPs deposited by DPN. The Au (MNN) transitions are labeled. Inset shows a 390 × 390 nm$^2$ SEM image of the C-Au NPs. Crosshair indicates point of analysis. (b) Derivatized Auger spectrum of an AFM tip inked with C-Au NPs. The C, O and Na peaks are labeled and are indicative of a trisodium citrate matrix surrounding the Au NPs.

Despite the significant amount of negatively-charged citrate ions comprising the ink, C-Au NPs were also successfully patterned on UVO-treated SiO$_2$ (Figure 2.8a), thereby demonstrating that negatively charged particles can be deposited via DPN on negatively charged substrates. As opposed to most DPN studies in which electrostatic attraction or covalent binding is required for patterning, the mechanism for Au NP patterning involves physisorption. Similar patterns were generated for both positively- and negatively-charged Au NPs on UVO-treated SiO$_2$. Therefore, these results
suggest that electrostatic attraction between Au NPs and the substrate surface is not necessary for patterning, presumably due to charge screening within the water meniscus. Under these experimental conditions, and assuming a water meniscus thickness of 1-2 nm [48] as the maximum Debye length, the minimum ionic strength of the C-Au NP solution flowing from the tip to substrate varies from ~25-100 mM, corresponding to a trisodium citrate concentration that is at least 2 orders of magnitude more concentrated than the original stock solution (which contained 0.04% trisodium citrate). This result also explains the codeposition of organic matrix observed in the aforementioned AES studies.

Subsequent experiments were performed to determine whether a highly hydrophilic surface is a key requirement for Au NP patterning. Indeed, no deposition of Au NPs was observed on moderately hydrophilic to hydrophobic substrates in the absence of covalent interactions. DPN of Au NPs on SiO\textsubscript{2} functionalized with pentafluorophenyl propyl trichlorosilane (static water contact angle $\approx 84^\circ$) did not result in deposition, even at RH as high as 70%. Furthermore, SiO\textsubscript{2} functionalized with mercaptopropyltrimethoxysilane (MPTS-SiO\textsubscript{2}, static water contact angle $\approx 45^\circ$) did not yield Au NP deposition unless the Au surface was available for covalent binding to the thiol groups. Only Nanogold particles were successfully patterned on MPTS-SiO\textsubscript{2}; DMAP- and C-Au NPs did not deposit on this surface because the Au surfaces were covered in an organic matrix and thus not accessible for thiol binding.

The Nanogold line patterns on MPTS-SiO\textsubscript{2} (Figure 2.8b) are almost an order of magnitude lower in height than those on UVO-treated SiO\textsubscript{2} (Figure 2.5), suggesting different mechanisms for Nanogold deposition on these two surfaces. The driving
force for Nanogold deposition on UVO-treated SiO₂ is Au NP dissolution and diffusion through the water meniscus to the hydrophilic surface. In contrast, the less hydrophilic MPTS-SiO₂ surface may result in a smaller water meniscus forming at the AFM tip/substrate interface, thereby limiting the dissolution of Au NPs absorbed on the AFM tip. The driving force for patterning is then covalent binding between surface thiols and Au NPs.

![Figure 2.8. AFM topographic images of C-Au NP line patterns on UVO-treated SiO₂ (a) and Nanogold line patterns on mercaptopropyltrimethoxy silane-treated SiO₂ (b). Scale bars: 2 µm.](image)

Further experiments were conducted to determine whether C-Au NPs could be patterned on single-walled carbon nanotubes – one of the eventual targets for nanostructured devices – absorbed onto aminopropyltrimethoxy silane functionalized surfaces based on electrostatic attraction between negatively-charged C-Au NPs and the positively-charged amino groups. An arbitrary region of the substrate was scanned using an inked tip, and the resultant image was uploaded to the InkCAD software for aligning boundary patterns to the ends of carbon nanotube bundles (Figure 2.9, left). After DPN of C-Au NPs at a relative humidity of 60%, the patterned region was imaged with a clean tip to reveal that no NPs were deposited (Figure 2.9, right).
Instead, the patterning process cleared away any carbon nanotubes in the path of the scanning tip; however, the tip contact force was 0.5-2 nN, which is several orders of magnitude lower than that required for shaving of the amino-silane [87, 88]. Therefore, the amino-silane should still be intact. The absence of patterned C-Au NPs further confirms that charge screening is occurring in this ink-substrate system due to the high ionic strength of the C-Au NP matrix at the tip. It should be noted in Figure 2.9 that there exists an offset of the designed patterns from the actual patterns (~1 µm in the +x-direction, and ~500 nm in the +y-direction). This offset seems to be due to a software limitation and its implications for electrical contact fabrication are discussed in Section 3, which explores an alternative patterning method since these amino-silanated surfaces (static water contact angle ≈ 65°) are not hydrophilic enough for DPN of Au NPs.

![Figure 2.9. (Left) An LFM image of carbon nanotubes on amino-silanated SiO$_2$. The grid lines (pitch = 1 µm) were used to register the blue boundary patterns to the ends of the carbon nanotube bundles. (Right) An AFM topography image of the same region after DPN.](image)

To verify that the relatively high contact angle of the amino-terminated surface was the cause for lack of patterning, DPN of C-Au NPs was attempted on amino-
terminated SiO$_2$ without absorbed carbon nanotubes. Indeed, no Au NPs were deposited, which is in contrast to nanofountain probe studies [74]. The nanofountain probe patterned a liquid residue (consisting of trisodium citrate) along with C-Au NPs, which were within an order of magnitude of the concentration of C-Au NP stock solution that needed to be concentrated for DPN. These results suggest that it is possible to tune ink-substrate interactions by adjusting the ionic strength of the Au NP ink. DPN of Au NPs can be made sensitive to electrostatic interactions by ensuring that the ionic strength of the ink is low enough such that charges are not screened. On the other hand, as seen in this study, the ionic strength of the DPN ink can be increased to enable deposition on arbitrarily charged, hydrophilic surfaces. These conclusions are consistent with reports on the importance of the water meniscus for ink transport in DPN [41, 50, 51, 86]. Therefore, a highly hydrophilic surface is required for DPN of Au NPs, unless covalent binding can occur between the Au NPs and the substrate surface, or the ink ionic strength can be sufficiently lowered so as not to screen substrate surface charges.

In an attempt to increase the density of Au NPs deposited with DPN (i.e., decrease the spacing between Au NPs), experiments were conducted with C-Au NP and MgCl$_2$-treated SiO$_2$. Our hypothesis was that these MgCl$_2$-treated substrates are still very hydrophilic (contact angle $\approx 0^\circ$) as in the case of UV-ozone and poly-L-lysine-treated SiO$_2$; however, the ability of citrate ions in the Au NP matrix to chelate Mg cations could shift the ink dissolution kinetics towards Au NPs sticking on the substrate more so than in the case of only electrostatic attraction to poly-L-lysine-treated SiO$_2$.  

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SiO₂ surfaces were treated with MgCl₂ through exposure to an aqueous 1 M MgCl₂ solution for 10 min. and a subsequent rinse with deionized water. DPN of C-Au NPs at RH of 67% resulted in sporadic deposition of aggregates as large as 60 nm, as shown in Figure 2.10; however, Au NP density did not increase presumably due to charge screening in the C-Au NP ink.

![Figure 2.10. AFM topography image of C-Au NP line patterns on MgCl₂-treated SiO₂.](image)

### 2.4.2.2. Ink-AFM Tip

Surface modification of AFM tips has been shown to facilitate DPN of biomolecules by increasing ink loading [89]. In order to reduce the charge screening in the Au NP ink yet still have enough Au NPs on the AFM tip for DPN, the surface of a tip was modified by coating alternately with C-Au NPs and poly-L-lysine in a layer-by-layer manner for a total of 6 layers. Poly-L-lysine was used as a cationic surfactant with a high solubility in aqueous solution. The incubation time for each layer was 3 min., after which the tip was dried with N₂ gas; this approach was used to prevent coating the tip with excess trisodium citrate ions, and the timescale is sufficient for adsorption of positively charged poly-L-lysine onto the negatively charged C-Au NPs.
[90]. However, subsequent DPN on a UVO-cleaned SiO$_2$ substrate at RH of 60% did not result in any deposition. An SEM of the inked tip (Figure 2.11) reveals scarcely any Au NPs compared to tips inked via the additive process discussed in Section 2.4.1 and used throughout this study. Perhaps using a higher concentration of poly-L-lysine (> 1 ppm) could result in more Au NP loading.

![Figure 2.11. SEM image of AFM tip inked alternately with C-Au NPs and poly-L-lysine.](image)

2.4.3. Relative Humidity

To further investigate the role of water in DPN of Au NPs, multi-pen experiments under various relative humidity conditions were performed. Using an AFM probe with multiple tips (shown in Figure 2.12a) allowed for a high-throughput evaluation of RH effects while taking into account potential variations in the inking of each tip (discussed in Section 2.5.1). In these nine experiments done in parallel, no Au NPs deposited at RH below 40%. All pens began patterning single-particle lines at RH 40%; a representative AFM image is shown in Figure 2.12b. As RH increased to 60% and patterning progressed, the height and line-width of patterns also increased as Au
NP aggregates were deposited and tip blunting occurred due to prolonged contact with the surface (Figure 2.12c). At RH of 70%, co-deposition of the solvent matrix was observed (Figure 2.12d). A larger water meniscus at higher relative humidity [48, 50] contributed to matrix deposition. Therefore, the optimal range for patterning Au NPs is RH of 40-60%. This optimal range was observed even for DMAP-Au NPs, which were not in aqueous solvent.

2.4.4. Writing Speed

The start-and-stop deposition of partial patterns (Figure 2.12d) indicates that DPN of Au NPs is an inhomogeneous process. Further evidence for this inhomogeneity is the fact that deposition is independent of writing speed or tip dwell time. No correlation between tip dwell time and Au NP deposition could be found for times ranging from 20 s to 120 s (Figure 2.13). Therefore, a diffusion coefficient could not be calculated for the transport of Au NPs from the tip to the substrate surface. Unlike inks such as small molecules and polymers, Au NPs do not spread laterally on substrates with increasing contact times. Single Au NPs were observed to deposit at dwell times of
both 1 s and 120 s. The Au NPs may stick on transfer and form a physical barrier against further deposition. Indeed, repeated writing of the same lines did not result in increased deposition of Au NPs.

![Figure 2.13. Plot of the measured heights of Au NPs in Figure 2.6 versus their respective tip dwell times. The data indicate that the amount of Au NPs deposited does not depend on tip dwell time for times ranging from 20 s to 120 s.](image)

For line patterns, writing speeds ranging from 0.01 to 2 µm/s also did not have any correlation with Au NP deposition. As discussed in Section 2.4.2, Au NPs exhibit a consistent diffusion profile with smaller particles depositing first followed by progressively larger particles as patterning proceeds. This phenomenon is illustrated in Figure 2.14 as writing speed is held constant at 1 µm/s. The discontinuities in Au NP deposition may be due to the time required for the particles to diffuse from the sides of the tip to the apex. A closer examination of the SEM image of an inked tip (Figure 2.3b) reveals islands of Au NPs that may contribute to the lag times in deposition. The variable particle sizes within each line in Figure 2.14 are also indicative of inhomogeneous deposition. Optimization of the Au NP ink is necessary to achieve more uniform coating of the AFM tip and homogeneous Au NP deposition.
Figure 2.14. AFM topographic images of C-Au NPs patterned on poly-L-lysine-treated SiO$_2$. Lines were written at the same speed of 1 µm/s, and patterning progressed from left to right. Scale bars: 1 µm.

2.4.5. Ink-Solvent Systems

Preliminary experiments with different ink-solvent systems were conducted to investigate their effect on ink loading and subsequent deposition. Hexanol was added to DMAP-Au NPs in a 1:1 ratio to investigate its potential as a lubricating agent since it has a higher boiling point than methanol (151.4 °C versus 64.7 °C). The resultant DPN-generated patterns consisted only of the solvent matrix (Figure 2.15). In another experiment, varying concentrations of ethylene glycol (boiling point: 197.3 °C) were added to C-Au NPs. At 10% incorporation of ethylene glycol, only the solvent matrix was deposited and evaporated over time (Figure 2.16). No Au NP deposition was observed for 1% ethylene glycol incorporation either. Au NPs were only patterned when there was 0.1% or less ethylene glycol present in the ink. This small percentage of ethylene glycol did not significantly affect the patterning of Au NPs. Other ink-
solvent combinations, however, could potentially result in more homogeneous patterning. In fact, studies in the literature have used surfactants for assisting DPN of biomolecules [91].

Figure 2.15. AFM topographic image of matrix deposition produced by DPN of DMAP-Au NPs in methanol/hexanol on UVO-treated SiO$_2$. Scale bar: 2 µm.

Figure 2.16. AFM topographic images of matrix deposition produced by DPN of C-Au NPs in 10% ethylene glycol. The pattern evaporates over time: (left) right after patterning, (middle) 30 min. after patterning, (right) 2 hrs after patterning.

2.5. **Patterning Issues**

2.5.1. Tip-to-Tip Variation in Gold Nanoparticle Deposition

High-throughput DPN of Au NPs *via* the multi-pen array is limited by the tip-to-tip variation in patterning, as seen in Figure 2.17, which plots the amount of deposition at
different RH levels for each of the nine pens in Figure 2.12a (numbered 1-9 from left to right). At RH 40%, pens 1-5 produced only partial patterning of Au NPs, whereas pens 6-9 produced complete patterning. The right side of the pen array (pens 6-9) may have produced better patterning due to initial contact with the substrate, despite optical leveling of the entire array prior to patterning. When RH was ramped up to 60%, only pens 7 and 9 deposited Au NPs. When RH was decreased to 50%, none of the pens deposited Au NPs; therefore, as ink is depleted from the tip, the RH needs to be ramped up for continuous deposition. Patterning resumed for about half the pens when RH was increased to 70%.

Figure 2.17. Plot of Au NP deposition for each of the nine pens on the DPN probe at various relative humidities as patterning time increases. The half-filled circles denote partial patterning and the black circles denote complete patterning.

SEM analysis of all pens after patterning suggests that the discrepancy in deposition was due to variable contact between the pens and substrate surface. For instance, pens 3 and 5 were blunter than pens 1, 2 and 4 (Figure 2.18). This variable contact seems to be inherent in the microfabrication of the probe pen array; however, the variation in patterning may be reduced by applying a higher setpoint (contact force) during writing.
or coating the tips with polydimethylsiloxane as in polymer-pen lithography, which has been shown to produce more uniform patterning than DPN [92].

Figure 2.18. SEM images of AFM tips after Au NP patterning in multi-pen RH experiment. Pens 3 and 5 have blunter tips and produced correspondingly more Au NP deposition than pens 1, 2 and 4. Scale bars: 2 µm.
2.5.2. Tip Shape Determination of Pattern Dimensions

At the lower range of RH (40-50%), where the water meniscus width is confined to the apex of the AFM tip, Au NP pattern dimensions were determined by the tip shape. Patterning of individual Au NPs is limited by the bluntness of the AFM tip, as seen in Figure 2.19, further confirming the absence of lateral surface diffusion in this ink-substrate system. This stamping effect is not seen for higher RH (60-70%), where the water meniscus is wider and Au NPs seem to diffuse from the sides of the AFM tip. Therefore, in order to achieve individual Au NP patterns, the AFM tip must be sharp (same order of magnitude as the Au NP diameter) and the RH at 40-50%.

![Figure 2.19](image.png)

Figure 2.19. (Left) AFM topography image of a series of Au NP dot patterns. (Right) High-resolution scan of one of these dot patterns, revealing a triangular shape due to the blunt patterning tip.

2.5.3. Driving Deposition with Applied Bias

In an attempt to overcome the tip-to-tip variations in patterning and control deposition independent of tip geometry, an electrochemical gradient was formed in the water meniscus between a negatively-biased AFM tip inked with C-Au NPs and a bare Si substrate. Our hypothesis was that the negatively charged citrate ions surrounding the Au NPs would be electrochemically driven to the positively-biased substrate.
Negatively charged Au NPs were used because otherwise a positively-biased tip would result in oxidation of the Si surface [79], making it more difficult to verify Au NP patterning. This setup could potentially enable deposition of Au NPs onto substrates with a wider variety of surface properties, e.g., hydrophobic substrates.

Since the AFM tip needed to be conductive, a Si tip was used in tapping mode; the setpoint and drive amplitude were increased to -0.1 V (80% increase) and 0.81 (4 X increase), respectively. The patterning results at RH 57% are shown in Figure 2.20: the ink solvent matrix was deposited, however, without Au NPs. The citrate ions may have dissociated from the Au NP surface. Experiments using Au NPs in which the negatively charged ligand is covalently linked to the surface (e.g., a negatively charged thiol such as mercaptoundecanoic acid or (3-mercaptopropyl)sulfonate) may result in deposition of Au NPs.

![Figure 2.20. AFM phase images of DPN-deposited solvent matrix right after patterning (left) and 20 min. after patterning (right). Height of film is 2-3 nm.](image)

### 2.6. Electroless Growth of Gold Nanoparticles

DPN-patterned Au NPs need to be grown into conductive wires or thin films in order to be useful as electrical contacts. However, codeposition of organic matrix inhibited electroless growth of the Au NPs. After a 2 min. exposure to GoldEnhance
solution, the average height of DPN-patterned C-Au NPs increases from 6 nm to 8 nm (Figure 2.21), which is only a 33% increase compared to the 100% increase observed for Nanogold particles (Figure 2.5). After an additional 4 min. of exposure to GoldEnhance, background autonucleation of Au NPs is apparent and some of the Au NPs in the line pattern are stripped away, possibly due to the rinsing steps. Therefore, despite being able to pattern C-Au NPs on any hydrophilic surface, the absence of electrostatic attraction between the Au NPs and the substrate results in loss of pattern fidelity in subsequent wet processing steps.

Figure 2.21. AFM topography images of DPN-patterned C-Au NPs on UV-ozone treated SiO$_2$: after patterning ($t=0$) and after 2 min. and 6 min. exposure to GoldEnhance solution.

To anchor the C-Au NPs on the substrate during solution processing, C-Au NPs were patterned on poly-L-lysine-treated SiO$_2$. Figure 2.22 shows that after 10 min. exposure to GoldEnhancement and rinsing, the patterned C-Au NPs are still present on the surface. One should note that background autonucleation did not occur in this sample. Subsequent experiments with GoldEnhance revealed that autonucleation tends to occur on bare SiO$_2$ after multiple exposures; therefore, it is recommended to expose the substrate only once to GoldEnhance solution for the desired incubation time.
The minimal growth of DPN-patterned C-Au NPs led us to try thermally annealing patterns at 200 °C for 20 min. before exposure to GoldEnhance for 10 min. The organic matrix was successfully burnt off, as evidenced by the 300% increase in average Au NP size (Figure 2.23). However, the problem of inhomogeneous Au NP size remains (see height profile in Figure 2.23), preventing the formation of a continuous Au nanowire for electrical contacts.

Figure 2.22. AFM topography images of DPN-patterned C-Au NPs on poly-L-lysine-treated SiO₂ before (left) and after (right) exposure to GoldEnhance solution. Pattern width is 2 µm.

Figure 2.23. (Left) AFM topography image of DPN-patterned C-Au NPs on poly-L-lysine-treated SiO₂ after thermal annealing and exposure to GoldEnhance solution. The triangular shapes of the patterns are an artifact of the blunt scanning tip. (Right) Corresponding line profile.
2.7. Direct Patterning and Reduction of Gold Salt

To circumvent limitations in electroless enhancement, we conducted electrochemical-DPN (E-DPN) of Au salt to effect a direct reduction into metallic Au on the substrate. E-DPN has been demonstrated for the deposition of various metals on Si coated with native oxide, achieving line widths of 30 nm [78]. Since the variation of pattern size with writing speed was not characterized, E-DPN of Au salt was conducted at various writing speeds on an Si substrate. An AFM tip was dipped into a 10:1 (vol.:vol.) mixture of acetonitrile and an aqueous solution of 20 mM AuCl$_4^-$ . The setpoint for writing was 0 V, and a positive bias of 1 V was applied to the AFM tip. The resultant line patterns are shown in Figure 2.24a; no correlation between speed and size of the Au nanowires was determined. The line widths remained at 150-200 nm even at faster writing speeds of 0.6 and 1 µm/s.

Figure 2.24. (a) AFM error image of line patterns from E-DPN of Au salt: writing speeds from left to right are 0.08, 0.06, and 0.04 µm/s. Line widths and heights are 150-200 nm and 2-4 nm, respectively. (b) AFM error image of a line pattern across microscale Au electrodes written with E-DPN of Au salt. The features on the Au electrodes are 600 nm in width and 100 nm in height. The gap between electrodes is 10 µm.
In order for this technique to be useful for making electrical contacts, we tried E-DPN of the Au salt on 300-nm thick SiO$_2$/Si substrates containing microscale patterned electrodes. However, Au nanowires were mainly formed on top of the microscale Au electrodes; only a faint line (height 0-5 nm) was observed in the channel region (Figure 2.24b). This minimal amount of patterning has been observed before with E-DPN of Pt resulting in line patterns less than 1 nm in ht [78]. The amount of patterning did not increase even when we decreased the writing speed from 0.6 to 0.01 µm/s and increased the bias from 1 to 4 V, further verifying the results on the Si substrate of lack of control over feature size via writing speed. This minimal amount of Au deposition was not suitable for application as electrical contacts.

### 2.8. Direct Patterning of Silver Ink

Since Au NPs are relatively bulky with an inhomogeneous diffusion profile compared to the molecular inks usually used in DPN, an alternative conductive ink based on silver acetate was evaluated. We hypothesized that this more fluid-like ink could be reduced in situ to form electrical contacts. An ink solution consisting of silver acetate, ethanolamine, and oleic acid in n-butanol was prepared according to a published procedure for spin-casting conductive Ag films [93]. However, it was found that this solution needed to be filtered every 15 min. or so to obtain clear yellow solution, thereby limiting the working time for DPN. The reduction of silver acetate occurs slowly to form Ag NPs. DPN with this ink at RH of 60% resulted in initial deposition of micron-sized features on SiO$_2$; however, no nanopatterning of Ag NPs was observed (Figure 2.25). Since photochemical reduction of silver is well
documented [94], scattered light from the AFM laser may also have accelerated the formation of Ag NPs on the patterning tip, thereby precluding DPN of the silver precursor. Another study in the literature describes DPN of Ag NPs; however, these patterns were not conductive (yielded sub-picoAmp current) [95].

Figure 2.25. (a) Optical image of silver ink deposited by attempted DPN. Dotted-square denotes scan area for AFM topography image (b). (c) High-resolution AFM scan of Ag NPs.

2.9. Conclusions

We have developed a procedure for loading sufficient amounts of Au NPs onto AFM tips for patterning on various surfaces, which either need to be highly hydrophilic or covalently bind Au for the ink-substrate systems in this study. This surface property limitation is most likely due to charge screening within the DPN ink that precludes electrostatic interactions between the ink and substrate. The Au NPs have a diffusion profile consistent with the Stokes–Einstein equation and, unlike other DPN inks such as 16-mercaptohexadecanoic acid, Au NPs do not diffuse laterally on the substrate surface during deposition. The patterns were verified as Au NPs using chemical development of the Au and elemental analysis via AES. Patterning only occurs at RH ≥ 40%, with the optimal range being 40% to 60%, and is not sensitive to writing speeds ranging from 0.01 µm/s to 2 µm/s. Further developments in the
formulation of Au NP inks and possibly surface modification of AFM tips are necessary to achieve more uniform coating of the tips and more homogeneous Au NP deposition. The difficulties in controlling the amount of deposition and the stringent surface chemistry requirements led us to pursue a different method of forming electrical contacts, discussed in the next chapter. However, this technique can be used to precisely place Au NPs onto substrates for the catalytic growth of carbon nanotubes [96], Ge nanowires [97], and Si nanowires [98], thereby fabricating interesting device structures from the bottom up. Furthermore, Au NPs can be used as highly sensitive single-molecule sensors for surface enhanced Raman spectroscopy [99].
3. Indirect Patterning of Electrical Contacts to Single-Walled Carbon Nanotubes (SWNTs)

This chapter discusses a method for the patterning of Au electrodes at nanoscale resolution using dip-pen nanolithography, with proof-of-concept demonstrated by creating single-walled carbon nanotube (SWNT) devices. Section 3.1 discusses the motivation for DPN of contacts to SWNTs as an alternative to electron-beam lithography (EBL). The experimental design and materials and methods are presented in Sections 3.2 and 3.3. Briefly, electrical contacts to individual and small bundle single-walled carbon nanotubes were masked by an alkanethiol that was deposited via dip-pen nanolithography on a thin film of Au evaporated onto spin-cast, non-percolating, and highly isolated single-walled carbon nanotubes. A wet Au etching step was used to form the individual devices. The optimization of these process steps is discussed in Sections 3.4 and 3.5, and the quality of the DPN-patterned contacts is discussed in Section 3.6.

The electrical characteristics for three different single-walled carbon nanotube devices – semi-metallic, semiconducting and metallic – are reported in Section 3.7. Raman analysis on representative devices (Section 3.8) corroborates the results from AFM imaging and electrical testing. The yield of DPN-patterned devices is evaluated in Section 3.9, and conclusions and supplemental information are discussed in Sections 3.10 and 3.11, respectively.

This work demonstrates a technique for making electrical contact to nanostructures of interest and provides a platform for directly corroborating electrical and optical measurements for the same isolated nanostructure. The merits of using dip-pen
nanolithography include flexible device configuration (such as varying the channel length and the number, size, and orientation of contacts), targeted patterning of individual devices with imaging and writing conducted in the same instrument under ambient conditions, and negligible damage to single-walled carbon nanotubes during the fabrication process.

This work has been published in *ACS Nano* [100]. Wechung Maria Wang wrote the paper and performed all the research and data analysis, except for the following: Raman analysis was conducted by Melbourne LeMieux, and parylene shadow masks were provided by Selvapraba Selvarasah.

### 3.1. Background

The conventional method of fabricating single nanotube devices for fundamental studies has been EBL [16, 101-103]; however, exposure to electron irradiation can damage SWNTs [104-108], thereby preventing measurement of intrinsic properties. This study introduces an alternative method for fabricating SWNT devices via DPN. The advantages of such an approach include selective placement and design of electrical contacts, targeted device fabrication (versus random selection as in EBL of predefined contacts), minimal damage during the fabrication process (no electron irradiation), and imaging SWNTs and patterning contacts in one system under ambient conditions. Patterning of contacts to individual SWNTs via EBL usually involves a prior AFM step to locate the targeted SWNT relative to alignment markers [109] or patterned growth of SWNTs via chemical vapor deposition (CVD) between predefined
electrodes and using an AFM tip to mechanically or electrically reduce the number of SWNTs bridging the electrodes to one [110].

DPN of 16-mercaptohexadecanoic acid (MHA) has been used to generate an etch-resist layer on Au films for patterning Au nanostructures on silicon [111-117]. This study optimizes the aforementioned MHA-masking method toward fabricating Au contacts to arbitrary arc-discharge SWNTs. Arc-discharge SWNTs were used due to their bulk production and solution processability being relevant to electronic applications. Au was used as the electrically contacting material and has been shown to make ohmic contact to carbon nanotubes operating as p-type transistors [118]. MHA remains on the Au contacts after fabrication and may affect the electrical characteristics of SWNT devices [119]; however, the MHA may be removed by annealing the substrate at sufficiently high temperatures [120] or by exposure to a NaBH₄ solution [121].

3.2. Experimental Design

This straightforward device fabrication technique (Figure 3.1) allows for electrical measurements on SWNTs with various dimensions and chiralities. The substrate is prepared by spin casting a dilute solution of SWNTs onto SiO₂/Si functionalized with an aminosilane to promote absorption. A thin film of Au (~15 nm) is thermally evaporated onto the substrate, either on top of photolithographically-patterned Au electrodes (as shown in Figure 3.1) or under Au electrodes to be patterned via a parylene-C shadow mask (obtained from our collaborators at Northeastern University). An AFM tip inked with MHA is used for rapid imaging of the SWNTs
under the thin film of Au and eventually masking contacts to the ends of an arbitrary SWNT. Finally, the substrate is immersed in a wet Au etchant to form the SWNT device.

![Schematic of SWNT device fabrication.](image)

The challenges in developing this method included optimization of the Au film, making it thick enough to be conductive yet thin enough so that AFM scanning could detect the SWNTs underneath. Furthermore, the diffusivity of MHA was optimized to obtain reliable patterns for electrical contacts (e.g., no shorts, clean etch) and two types of Au etchant were evaluated for comparison of etch quality. Challenges in
forming reliable electrical contact between the MHA-masked Au and the larger Au electrodes used for electrical probe measurements led to development of two device fabrication routes. Finally, electrical characterization and Raman analysis of different types of SWNT devices were conducted to validate this fabrication method.

3.3. Materials and Methods

3.3.1. Surface Preparation

Substrates consisted of heavily doped silicon wafers with 300-nm thermally grown oxide layers (Silicon Quest International) diced into centimeter-sized pieces. All substrates were cleaned for at least 20 min. in a UV-ozone cleaner (Model 42, Jelight Company, Inc.) before further surface modification. Amine functionalization of SiO$_2$ occurred through solution deposition of 1 vol. % aminopropyltrimethoxy silane (Gelest, Inc.) in toluene for 1 hour, followed by sonication and rinsing in toluene and drying under N$_2$. The contact angle of the resultant amine surfaces was 68° ± 2°.

3.3.2. Spin Casting of Carbon Nanotubes

Solutions of arc-discharge single-walled nanotubes (average length of 1 µm) were obtained following a method described previously [122]. These carbon nanotube solutions were diluted to 1 µg/mL in NMP (n-methyl-2-pyrrolidone, EMD) for spin casting, producing electrically isolated SWNTs on the substrate surface. Approximately 15 µL of the CNT solution was pipetted onto each substrate during spinning at 3000-4000 RPM (Headway Research). The substrates were then dried in a vacuum oven at 80 °C for approximately 1 hour to remove residual solvent. It is
important to note that purified SWNT solutions should be used to avoid deposition of Fe catalyst particles, which may serve as etch accelerant points. Furthermore, the SWNT solutions were periodically resuspended every month by exposure to ultrasonication for 10 min. at 20% amplitude.

3.3.3. DPN of MHA

A thin Au film (15-17 nm) was thermally evaporated (rate of 1 Å/s) on the substrates containing SWNTs for DPN of MHA (16-mercaptohexadecanoic acid, Sigma-Aldrich) masks. Au substrates can be stored under Ar or N\textsubscript{2} for at least one month before patterning. Patterning (contact mode, setpoint 1.5 to 2 V) and imaging (contact and AC mode) were performed on an NSCRIPTOR DPN system (Nanoink, Inc.) at ambient temperature (26 °C ± 4 °C) and relative humidity (30-50%).

MHA was inked onto the diving-board cantilevers of type A Si\textsubscript{3}N\textsubscript{4} probes (nominal spring constant 0.041 N/m) obtained from Nanoink, Inc. The AFM tips were dipped twice into 5 mM MHA in acetonitrile, once in deionized water, again into the MHA solution and finally into ethanol, with N\textsubscript{2} drying in between the dipping steps. MHA-inked tips were used for rapid imaging (speeds greater than 50 µm/s) of SWNTs for contact registration and patterning verification. Once a suitable SWNT was found, the scanned LFM or error image (scanning was too rapid for features to appear in topography image) was uploaded into the InkCAD software for design of contacts (boundary patterns) to the ends of the SWNT. Feature size was determined by a linear fit for “diffusivity” at the beginning of each patterning session via InkCal, a calibration tool built into InkCAD. This value is not the actual diffusion coefficient of
MHA on the surface, rather it is a relative value used for designing features of known dimensions.

3.3.4. Au Etching

A modified version of an acidic Fe(NO$_3$)$_3$/thiourea solution [123] was used for Au etching: 1:1 mixture of 26.6 mM Fe(NO$_3$)$_3$·9(H$_2$O) (J.T. Baker) and 40.0 mM thiourea (Alfa Aesar) in deionized water, adjusted to ~pH 2 using HCl (EMD). Au was etched in a reagent volume of 1.2 mL under constant stirring at 120 RPM for 6-7 min. at ambient temperature. Other studies in the literature add octanol to the etchant [124]; however, the addition of octanol only improves the selectivity of the etch when a hydrophobic SAM is used, e.g., octadecylthiol, which has been shown to be a less effective mask than MHA [113, 125, 126]. In the case of MHA, it should have a negligible effect, as observed in our experiments. The ferri/ferrocyanide etchant used for comparison studies was composed of 0.1 M Na$_2$S$_2$O$_3$, 1 M KOH, 0.01 M K$_3$Fe(CN)$_6$, and 0.001 M K$_4$Fe(CN)$_6$ [127]. Au was etched under constant stirring at 120 RPM for ~14 min. at ambient temperature. Substrates were then rinsed thoroughly in deionized water and dried with air.

3.3.5. Device Characterization

SWNT devices were imaged using Si probes obtained from Nanosensors, with nominal force constants of 42 N/m and nominal resonance frequencies of 320-330 kHz. AFM images were flattened using the Scanning Probe Image Processor (SPIP, Image Metrology A/S). Electrical measurements were conducted using a Keithley
4200 SC semiconductor analyzer. Prior to measurement, substrates containing photolithographically-patterned Au electrodes were annealed on a hotplate at 290 °C for 20 min. to ensure conductive Au contacts. The purified SWNTs are stable at this temperature; in the absence of transition metal impurities, the oxidation temperature of SWNTs in air is over 500 °C [128]. The applied source-drain bias was limited to a maximum of 100 mV to prevent electrical breakdown of the 15 nm-thick Au contacts. It was observed that these Au contacts can withstand up to 40 mA current before becoming insulating (see Appendix, Figure 3.16).

Micro-Raman (LabRam Aramis, Horiba Jobin Yvon) spectroscopy of SWNTs was conducted at 633 nm (1.96 eV) excitation with 1800 grating at 100X magnification, resulting in a ~700 nm spot size. Excitation power through the filter was 1 mW for the 633 nm line. It was determined that an intensity higher than 5 mW could burn the nanotubes over the acquisition period. The spectra were acquired via 10 × 10 (100 point) mapping in the vicinity of the DPN-patterned device channel (easily visible at 100X magnification), with two spectra acquired and averaged at each point. Since most of these mapping points resulted in “dead scans” with no SWNT present, these “flat” spectra were discarded for the statistical analysis. All summarized data were normalized to the 303 cm\(^{-1}\) mode in silicon.

### 3.4. MHA Diffusivity

A typical substrate for DPN is shown in Figure 3.2: the channel lengths to be bridged by MHA-masked contacts are 5 to 10 µm. The lateral force microscopy (LFM) image shows rectangular MHA patterns overlapping the ends of the SWNT
and the larger Au electrodes across a 5 µm channel. These boundary patterns were created using InkCAD software, which allowed for the specification of feature sizes based on MHA diffusivity. The optimal range of MHA diffusivity was found to be 0.02 to 0.05 µm²/s. For diffusivity lower than 0.02 µm²/s, the long patterning time resulted in vapor diffusion of MHA indiscriminately onto the substrate surface. For diffusivity higher than 0.05 µm²/s, the patterns also were not well-defined and often resulted in shorted devices, possibly due to formation of multilayers of MHA during patterning and/or deposition during scanning (Figure 3.3). The time required for DPN of a single device was 5-20 min., depending on channel length and contact configuration. In cases where carbon nanotubes operate as Schottky barrier transistors, the conductance can be modulated by the electric field at the contacts; therefore, the contact geometry can be optimized, e.g., designed to be sharper and thinner, to improve device performance [129].

Figure 3.2 (left) Optical image of a substrate with electrically isolated SWNTs and predefined Au electrodes beneath a thin film of Au. The area to be patterned by DPN is denoted with a blue circle. Scale bar is 40 µm. (right) LFM image of a SWNT after MHA masking of contacts to the predefined Au electrodes.
3.5. Evaluation of Gold Etchant Systems

After patterning the MHA-masking layer, the substrates were exposed to a gold etchant (details in Section 3.3.4). Two types of wet etchants that have been used for Au patterned with self-assembled monolayers (SAMs) [113, 130] were evaluated for their selectivity in preserving the MHA-masked Au. As shown in Figure 3.4, the ferric nitrate/thiourea etchant yielded a cleaner etch (fewer residual Au particles) and better pattern fidelity than the ferri/ferrocyanide etchant. The Au contacts in Figure 3.4a are less uniform and have a higher pinhole density compared to those in Figure 3.4b (see height profile insets). The SAM mask may have been undermined by the slower etch rate of ferri/ferrocyanide (~0.7 nm/min) compared to ferric nitrate/thiourea (~2.5 nm/min). Moreover, the charged thiosulfate species in the ferri/ferrocyanide etchant is more likely to penetrate the hydrated surface of the MHA SAM than the neutral thiourea species [125]. The higher selectivity of the ferric nitrate/thiourea etch led to its use in producing subsequent SWNT devices. Figure 3.5 shows different contact configurations to SWNTs after etching with ferric nitrate/thiourea. These patterns demonstrate the versatility of DPN in designing contact configurations for specific
types of SWNTs (e.g., depending on their orientation, size, single SWNT or junctions).

Figure 3.4. AFM topography images of MHA-masked Au contacts to SWNTs after etching in ferri/ferrocyanide (a) and ferric nitrate/thiourea (b). The blue lines denote line profiles of the height variation, shown in the insets.

Figure 3.5. (a) Optical image of a SWNT device. The distance between the larger Au pads is 5 µm. (b,c) AFM topography images of MHA-masked Au contacts to a single SWNT and a junction of two single SWNTs, respectively. Scale bars are 500 nm.

3.6. **Characterization of MHA-Masked Gold Contacts**

The MHA-defined Au served as electrical contacts between the ends of SWNTs and the larger Au electrodes, which were either photolithographically patterned under
SWNTs and a thin film of Au (as shown in Figure 3.2) or deposited via a parylene-C shadow mask [131] on top of the thin film of Au. The photolithographically-patterned Au electrodes were fabricated on a wafer scale and could be stored for future use when a fresh film of Au would be deposited on top for DPN. However, there were disadvantages to using the photolithographically-patterned Au electrodes. First, depositing a thin film of Au (10-15 nm) on top of thicker, predefined electrodes (35-40 nm) resulted in a discontinuity at the electrode edges due to the height barrier. Therefore, if the predefined electrodes were to be under the Au thin film, both depositions needed to be of similar thickness (15-17 nm, thin enough to image SWNTs underneath) and thermal annealing was required to obtain consistent conductivity. Furthermore, careful probing during electrical measurement was necessary so as not to pierce through the thin Au electrodes. Keithley probes would slip on the Au electrodes, presumably due to the presence of organic residue from the SWNT spin-coating process. Depositing the Au electrodes through a parylene-C shadow mask on top of the Au thin film circumvented these limitations. Moreover, if one end of a SWNT was already under an electrode, then only one top contact needed to be patterned with DPN, thereby halving the patterning time per device. Channel length as short as 5 µm was resolvable using the parylene-C masks when pressure was applied to laminate the mask to the substrate.

The conductivity of the MHA-masked Au contacts ranged from \(~4-5 \times 10^6\) S/m (Figure 3.6), which is the same as that measured for Au nanostructures fabricated via EBL [132]. Therefore, DPN is a comparable substitute for EBL in creating conductive Au contacts for nanostructured devices.
3.7. Electrical Characterization of Semiconducting, Semi-Metallic, and Metallic SWNT Devices

Besides ensuring that the DPN-generated contacts were conductive, it was necessary to show that this fabrication process did not damage the SWNTs. Therefore, a more concentrated (10X) SWNT solution was used to prepare a percolating network of SWNTs as thin-film field-effect transistors, which were then subjected to the same processing conditions of Au deposition and subsequent etching. Electrical characterization of these devices before and after processing yielded similar I-V characteristics (Figure 3.7), thereby demonstrating that this fabrication method does not alter the electronic properties of SWNTs and suggesting that the SWNTs have not been damaged.
The functionality of DPN-patterned devices was verified through electrical measurements on three different types of SWNTs: semi-metallic, semiconducting and metallic. To compare the performance of these devices with those reported in the literature, key figures of merit were calculated, such as the transconductance ($g_m = \frac{dI_{DS}}{dV_G}$) at a given source-drain voltage ($V_{DS}$) and the field-effect mobility for operation in the linear regime: $\mu = \frac{(L/V_{DS}C_g)(dI_{DS}/dV_G)}{L/W}$, where $L$ is the device channel length between the MHA-masked Au contacts and $C_g$ is the gate capacitance per unit length of the SWNT, estimated from $2\pi\varepsilon_{ox}/\ln(4t_{ox}/W)$, where $\varepsilon_{ox}$ is the effective dielectric constant of SiO$_2$ ($3.9\varepsilon_0$), $t_{ox}$ is the oxide thickness (300 nm), and $W$ is the diameter of the SWNT [16].

A semi-metallic SWNT device is shown in Figure 3.8; the device did not turn off, even at $V_G = 10$ V, yet the measured current was modulated by $V_G$. The AFM image reveals that this device consists of two nanotubes in a y-shaped junction. The calculated transconductance was $1.9 \times 10^{-8}$ S, which is an order of magnitude greater...
than that reported in literature for a single solution-processed SWNT with a similar
device structure (SiO$_2$/Si substrate with Au electrodes) fabricated via EBL [16]. The
higher transconductance may be due to this device being a two-tube bundle.

Figure 3.8. (a) AFM topography image of a semi-metallic SWNT device with the two-tube bundle
magnified in the inset (Z-scale is 3 nm), which also shows the optical image of the entire device.
The length of the SWNT section between the MHA-masked Au contacts is 600 nm. (b) Output
curves indicating semi-metallic behavior. (c) Transfer curve at $V_{DS} = -0.05$ V and sweeping from -10 to 10 V. The dashed red line denotes a linear fit for calculating the transconductance.

Figure 3.9 shows the measured I-V curves for the p-type semiconducting SWNT in
Figure 3.2. The on/off ratio was $\sim$4,000, and leakage current was in the picoamp range
with no dependence on $V_G$. The field-effect mobility was $\sim$23 cm$^2$/V·s ($W = 2$ nm, $L =
2$ µm), which is within the same order of magnitude as reported for solution-processed, single SWNTs in the literature [16, 133], as is the transconductance at $3.6 \times 10^{-9}$ S.

Another p-type semiconducting SWNT device is shown in Figure 3.10. The
residual Au seen in the AFM image is from an incomplete etch; the exposure time was
not long enough to etch all of the unmasked Au film, possibly due to a measurement
error in the thickness of the Au for that particular deposition. Nevertheless, the
calculated figures of merit for this device are within the same order of magnitude as
previous ones \( g_m = 5.9 \times 10^{-9} \text{ S} \) and \( \mu \approx 67 \text{ cm}^2/\text{V}\cdot\text{s} \) for \( W = 1.6 \text{ nm}, L = 1.86 \text{ \mu m} \).

The \( I_{DS,max} \) for this single SWNT device is much lower than for the bundle in Figure 5. Furthermore, repeated electrical measurements resulted in loss of conductivity probably due to breakdown of the tube [134]. Indeed, AFM imaging after additional Au etching revealed that a gap formed along the SWNT (inset in Figure 3.13c).

Figure 3.9. Output (a) and transfer (b) curves for the SWNT device shown in Figure 2, indicating p-type semiconducting behavior. The dashed red line denotes a linear fit for calculating the transconductance at \( V_{DS} = -0.1 \text{ V} \) as \( V_G \) sweeps from 20 V to -20 V.
A metallic SWNT device is shown in Figure 3.11. The current was not modulated by $V_G$, and the measured resistance was 130 kΩ, which is comparable to that measured in devices with low-resistance contacts fabricated via EBL [135]. Further evidence for the MHA-masked Au as low-resistance contacts is presented in Figure 3.12, which shows a short-channel metallic SWNT device ($L = 135$ nm) with a resistance of ~18 kΩ at room temperature, indicating that the MHA-masked Au is likely making ohmic contact to the SWNT [25, 118]. Therefore, this technique can potentially be used to probe the intrinsic electrical properties of SWNTs.
3.8. **Raman Analysis of Semiconducting and Metallic SWNTs**

To complement the electrical characterization, Raman data obtained from high-resolution spectral mapping of the SWNT devices were analyzed. The DPN-patterned devices were easily identified through optics in the Raman system, resulting in a very high probability of analyzing the specific SWNTs in the device channels. This attribute of the DPN-patterned electrodes is advantageous for the difficult experiment.
of obtaining electrical, topographical, and optical (structural) data from the same isolated nanotube. The conventional method of conducting such studies has involved using a more complicated experimental setup such as low-temperature scanning tunneling microscopy and scanning tunneling spectroscopy [136, 137]. Moreover, DPN offers the flexibility of writing to only the species of interest, in this case an individual tube and a bundle that exhibited different electronic properties, thereby providing a versatile method for comparing and understanding fundamental properties of nanotubes. Although directly correlated electrical and Raman measurements have been conducted previously on the same nanotube species, these studies lacked AFM topographical data [138] or were conducted on a single double-walled nanotube [139] or nanotube films [140, 141]. Recently, a method for directly correlating electrical and Raman data was reported for isolated nanotubes [142], but it involved transfer printing CVD-grown tubes onto a substrate with predefined electrodes, thereby lacking the flexibility of direct imaging and selecting SWNTs of interest displayed in this work.

Complete structural information on SWNTs can be obtained from Raman analysis. Raman imaging in the form of 100-point mapping was conducted on two of the DPN-patterned device channels. The resulting spectra were compiled and averaged (dead scans on Si with no nanotube signature were discarded) and are shown in Figure 3.13. Figure 3.13c shows the Raman spectra for a semiconducting SWNT that was electrically characterized (shown in Figure 3.10). The single peak in the RBM region (170 cm\(^{-1}\)) indicates that this device is composed of a single semiconducting SWNT, which agrees with the AFM and electrical data. The diameter of this nanotube...
observed with AFM is around 1.6 ± 0.1 nm, indicating that this SWNT could have a
chiral vector of either (18,2) or (14,10), which also corroborates with the RBM-
determined diameter through a previously developed equation relating wavenumber to
diameter for isolated SWNTs [143]. All scans from mapping on this device revealed
only the 170 cm\(^{-1}\) peak (refer to Appendix, Figure 3.15). On the other hand, for the
device characterized in Figure 3.11 showing metallic electrical behavior, the RBM
region (Figure 3.13d) indicates average spectra with both metallic and semiconducting
signatures from a SWNT bundle. In Figure 3.13d (and clearly seen in Appendix,
Figure 3.15), a metallic RBM peak is observed centered at 200 cm\(^{-1}\), most likely from
a (12,6) metallic tube with diameter around 1.3 ± 0.1 nm. The AFM-measured height
of the SWNT bundle is ~2.5-3 nm (approximately what is expected for a two-tube
bundle). Thus, both the AFM and Raman analysis for the reported metallic SWNT
device indicate that it is composed of a bundle. The peaks at ~135 cm\(^{-1}\) and ~149 cm\(^{-1}\)
are noise from air.
Figure 3.13. Raman spectral mapping of the DPN-patterned devices at 633 nm compiled from 10 × 10 (100 point) mapping. (a) Optical image (100X), with mapping points overlaid, of a typical DPN-patterned device for Raman characterization, with the scale in units of microns. The isolated nanotube bridges the gap between the MHA-masked Au at the closest point. (b) Resulting map image of the nanotube on the Si substrate, with contrast resulting from the intensity difference at ~1600 cm$^{-1}$ (G-band) between a spot with a nanotube or only Si (no peak at 1600 cm$^{-1}$). Scale bar is 100 nm. (c) Compiled average spectra in the RBM region of an individual semiconducting SWNT (pink and purple shading represent semiconducting and metallic transitions, respectively), along with AFM image (inset, scale bar is 500 nm, Z-scale is 5 nm). (d) Compiled average spectra in the RBM region of an isolated nanotube bundle displaying both semiconducting and metallic peaks, along with AFM image (inset, scale bar is 100 nm, Z-scale is 4 nm). (e,f) G-band region of the individual and bundled SWNT devices, respectively. The inset in (f) is a comparison of the two devices (normalized to the 303 cm$^{-1}$ Si line), showing the enhanced intensity and broadening of the G$^-\!$ band in the bundled sample.

In addition to the RBM region, the G-band region is also quite different for the two devices. Most notably, the G$^-\!$-band for the bundled sample is much more intense (inset, Figure 3.13f) due to the fact that two tubes are resonant rather than a single SWNT. Also, this band is broader than the corresponding G$^-\!$-band for the single SWNT, which has a Lorentzian shape, confirming that the single SWNT is semiconducting (clearly seen in Appendix, Figure 3.15). The peaks around 1325 cm$^{-1}$ result from defects in nanotubes (D-band), and this peak is relatively larger for the single SWNT. Since the SWNTs were solution processed, this larger peak could be a
result of the single tube becoming more damaged during sonication than the more rigid bundles. Another peak around 1440 cm\(^{-1}\) could be attributed to substrate effects [144] or possible organic (MHA) residue [145]. However, this peak has also been observed for ~1.5 nm-diameter, isolated semiconducting SWNTs in slightly bad resonance at 633 nm excitation [146], which could explain why it is stronger in the case of the device with the single SWNT.

### 3.9. Device Yield

The majority of the SWNT devices patterned via DPN in this study were composed of bundles or metallic tubes because these were easier to locate under the Au thin film due to their mostly larger diameters when compared to individual semiconducting SWNTs. One could also do an AFM scan before deposition of the Au film to locate individual, small diameter SWNTs. Knowledge of their location relative to alignment markers would allow for a higher yield of devices containing a single SWNT.

Another challenge in the DPN process was the offset of patterns by as much as 500 nm from the original InkCAD design, presumably due to a software issue. This problem usually was remedied by accounting for the offset in the design, e.g., making the width of the patterns at least 1 µm. The offset does not seem to be systematic, although most cases involve a ~500 nm offset in the +x direction and a negligible offset in the y-direction. Experiments were conducted to evaluate whether the offset is a factor of the (x,y) coordinates of the uploaded image, the pitch of the registration grid, overscan settings, scan resolution, or speed of scanning. Control of the
The yield of devices under optimized conditions was 60%, with the nonfunctional devices mostly due to the aforementioned registration error or overetching of Au contacts at the edges of the substrate (Figure 3.14). Rapid evaluation of patterned substrates by optical microscopy could reveal obvious nonfunctional devices due to overetching or incomplete contact to the larger Au pads. In the latter case, the lack of a yellow tint to the MHA-masked Au (indicative of a thicker Au film than the normally pink 15 nm film) overlapping the larger electrode pads signaled a discontinuity at the electrode edge. Occasionally, the MHA masking would be incomplete, presumably due to incomplete ink coverage of the patterning tip. This problem may be avoided by ensuring that the ink solution is fresh (< 6 months old) and has been sonicated before inking.
This device fabrication yield of 60% compares favorably to other techniques for studying solution-processed SWNTs, which are either randomly deposited onto electron-beam defined electrodes or flow-aligned. The latter method results in a higher yield of single SWNT devices, although even then the yield is only ~8% [133]. Subsequently, most SWNT reports in the literature use CVD-grown tubes, in which case targeted patterning to a single tube is limited by the geometry of the SWNT as determined with AFM scanning; SWNTs need to be elongated with length > 3 µm to account for the inaccuracies in electron beam lithography registration and alignment to the AFM-determined coordinates [109]. In contrast, DPN can be used to make contact to shorter SWNTs with lengths of at least 1 µm.

Figure 3.14. Process problems lowering device yield. (a) AFM topography image of misaligned MHA-masked contacts. This is an extreme case of misalignment by ~1 µm in both the +x, y directions. The intended SWNT for patterning is circled in black. (b) Bottom MHA-masked contact detached during the Au etching process. (c) Incomplete MHA patterning led to erosion of masked Au during etch. (d) Overetching of MHA-masked contacts due to edge effects of increased turbulence. (e) The discontinuity of MHA-masked contacts at the connection points to the larger electrodes (channel length is 5 µm) can be discerned by the absence of yellow-tinted Au at the edges. The channel lengths for (b-d) are 10 µm.

3.10. Conclusions

Several parameters were studied to enable DPN patterning of functional SWNT devices. The optimal range of MHA diffusivity was found to be 0.02 to 0.05 µm²/s for reliable patterning. The ferric nitrate/thiourea etchant yielded a cleaner etch and
better pattern fidelity than the ferri/ferrocyanide etchant. Two different device fabrication methods were used for patterning the larger Au electrodes that contacted the MHA-masked Au. The resultant SWNT devices were comparable to those defined by EBL; the conductivity of the MHA-masked contacts was $\sim 4.5 \times 10^6$ S/m and the I-V characteristics of SWNT thin-films before and after Au deposition and etching were shown to be similar. Furthermore, the measured SWNT transconductance values were on the order of $10^{-8}$ to $10^{-9}$ S, and the field-effect mobilities were consistent with literature reports for isolated, solution-processed SWNTs. Finally, Raman spectra corroborated the SWNT characteristics obtained from AFM and electrical data, and provided insight into the structure of the nanotubes comprising these devices.

DPN-patterned devices can be used to further elucidate the intrinsic electrical and structural properties of SWNTs under ambient conditions, e.g., enabling investigation of the effects of strain and surface chemistry on electrical properties of SWNTs [147], charge transport through junctions, and the effect of selective band gap engineering for nanoelectronics. Furthermore, other inks besides MHA can be used as the masking layer to tune the electrical characteristics of carbon nanotube devices [119]. The advantages of this technique for patterning such devices include selective placement and design of electrical contacts, targeted and rapid device fabrication, and mild and facile processing conditions.
3.11. Appendix

Figure 3.15. All spectra from typical Raman spectral mapping, with all ‘dead scans’ removed (scans on empty areas without any signal from nanotubes). For the semiconducting nanotube (top row), the RBM region (top left) shows only one peak (170 cm$^{-1}$), for all spectra, and it falls within the semiconducting (pink-shaded) region. This is in sharp contrast to the RBM region for the bundled system (bottom left), where distinct peaks are observed in both the semiconducting (170 cm$^{-1}$) and metallic (purple-shaded) regions (198 cm$^{-1}$). The peaks at ~135 cm$^{-1}$ and ~149 cm$^{-1}$ are noise from air. The G$^-$ band for the bundle (bottom right) is much broader than in the case of the individual tube, for which a mostly Lorentzian shape is observed (top right).

Figure 3.16. Optical images of MHA-masked Au contact before (left) and after (right) electrical testing at a source-drain bias of 1.5 V. Channel length is 10 µm.
4. **Indirect Patterning of Electrical Contacts to Graphene Nanostructures**

This chapter discusses the application of the DPN masking method toward making electrical contacts to monolayer graphene. Section 4.1 evaluates current methods for fabricating graphene devices and motivates DPN as an alternative method. The experimental design and materials and methods are presented in Sections 4.2 and 4.3. Results of isolating monolayer graphene, subsequent patterning of contacts and electrical characterization are discussed in Sections 4.4-4.6.

The higher resistivity values of DPN-generated graphene devices versus those fabricated via electron-beam lithography (EBL) led us to investigate possible damage to the graphene from processing. Indeed, damage was inflicted on the graphene flakes during Au deposition and subsequent etching (Section 4.7.1) and nanoparticle (NP) residue remained on the graphene after processing (Section 4.7.2). Although the Au masking layer is an inherent component of this process, it may be possible to eliminate the NP residue through a protective sacrificial layer on top of the graphene (Section 4.8). To circumvent this issue, DPN patterning of contacts to reduced graphene oxide nanoplatelets was attempted (Section 4.9). However, no conductance was measured through the resultant devices. The limitations of this DPN process for contacting graphene and the conclusions of this study are discussed in Section 4.10.

The exfoliated graphene samples were provided by Kathryn Todd and Nimrod Stander in the Goldhaber-Gordon group at Stanford.
4.1. **Background**

The established method for fabricating graphene devices is as follows. First, graphene flakes are produced by mechanical exfoliation of graphite and deposited on a highly doped Si substrate, covered by 300 nm of oxide. This oxide thickness is key to being able to locate monolayer graphene with optical microscopy. Raman spectroscopy is then used to confirm the single-layer nature of the flakes. The monolayer graphene is then isolated from the rest of the multilayered flake by EBL and reactive ion etching. Finally, contacts are added using a second EBL step and metal evaporation [148]. Exposure to electron beam irradiation during any of these steps (EBL or SEM imaging) may damage the graphene [149].

This study replaces the EBL steps with DPN, a simpler and mild process that has been shown to produce SWNT devices of comparable performance to those fabricated *via* EBL (Section 3). Since EBL usually uses a positive resist (regions of the photoresist exposed to light are removed) and DPN acts as a negative resist (patterned regions are masked), less patterning is required to isolate the monolayer graphene from the larger multilayer regions when using DPN. Furthermore, it is easier to use DPN to define nanoribbons and other arbitrary nanostructures of graphene due to the registration limits of EBL with a positive resist. The goals of this study included evaluating the translation of the DPN process from the SWNT system to graphene and comparing the performance of the resultant devices to those fabricated *via* EBL.
4.2. **Experimental Design**

The major challenges in adapting the DPN process toward graphene device fabrication included defining monolayer graphene flakes, ensuring flake adhesion to the substrate during the Au etching process, and alignment of larger contacts to the flakes. Since the bulk of this study dealt with exfoliated graphene, which mostly consists of multilayers, it was necessary to isolate the monolayer regions of graphene for device fabrication. Figure 4.1 illustrates the process steps involved in defining monolayer graphene. First, a 10 nm film of Au is thermally evaporated onto the exfoliated graphene on SiO$_2$ treated with an adhesion layer. This film is slightly thinner than the one used in the SWNT study so that AFM scanning could detect the thinner graphene flakes underneath. Next, DPN of 16-mercaptohexadecanoic acid (MHA) masks the single-layer graphene, leaving the rest of the multilayer graphene flake exposed after Au etching. An O$_2$ plasma treatment is then used to etch away the exposed graphene layers. Furthermore, the O$_2$ plasma has removed the MHA mask, leaving the Au film susceptible to wet etching, thereby revealing the isolated monolayer of graphene.
Figure 4.1. Schematic of graphene device fabrication.

The next processing steps are similar to those reported for SWNT device fabrication in Section 3.2, with the important exception of having to align larger electrodes *via* a parylene-C shadow mask to the defined graphene flake. In the case of SWNT device fabrication, the SWNTs were selected for patterning based on their location within predefined channels between electrodes. However, in the case of graphene, usually only one monolayer flake was found and defined per substrate due to the low yield of the exfoliation step. Therefore, it was necessary to position the larger gold electrodes such that the graphene flake lay within the channel region. The challenges associated with this step are discussed in Section 4.3.4.
4.3. **Materials and Methods**

4.3.1. **Substrate Preparation**

Exfoliated graphene was deposited on hydrophobic SiO$_2$ using a previously published procedure [150]. The SiO$_2$ surface was rendered hydrophobic because previous studies with a hydrophilic surface from piranha-cleaning resulted in delamination of graphene during solution processing. Therefore, a hydrophobic self-assembled monolayer (SAM) was used to promote graphene adhesion to the SiO$_2$ substrate. It was also of interest to our collaborators to study the passivating effects of such SAMs on the SiO$_2$ in reducing trapping sites for charge transport, thereby increasing the charge carrier mobility [151].

Various SAMs were screened for graphene adhesion: 1) octadecyltrichlorosilane, 2) 2-cyanoethyltriethoxysilane, 3) 3-mercaptopropyltriethoxysilane, 4) phenyltriethoxysilane, 5) dodecyltriethoxysilane, 6) cyclopentyltrichlorosilane, 7) bromophenyltrichlorosilane, and 8) n-octyltrichlorosilane. Graphene was found only on SAMs #1, 4, 5, 7 and 8. Since the yield is rather low, only 1 chip out of 4 had graphene on it for each SAM, it is difficult to conclude whether certain types of SAMs are more suitable than others for graphene adhesion. The SAMs onto which graphene did adhere either contain a long alkyl chain or an aromatic group facing the graphene. Devices were fabricated with exfoliated graphene deposited on SAM #5 only. For the preliminary experiments with reduced graphene oxide, the graphene oxide platelets were spin-coated onto bare SiO$_2$ following a previously published procedure [152].

For experiments on the reduction of nanoparticle residue on graphene, a protective, sacrificial polymer layer was spin-coated on the substrate before deposition of the thin
Au film (10 nm). High and low molecular weight polystyrene (PS, Polymer Source) was used for exfoliated graphene since the SiO$_2$ was functionalized with a hydrophobic SAM. Solutions of PS/toluene were prepared by weight in concentrations of 0.5 wt.% for $M_n = 88,000$ and 0.5, 1, and 2 wt.% for $M_n = 8,000$. Substrates were then flooded with the polymer solution, accelerated to 4000 RPM in less than 2 s, and left spinning for 60 s [153]. After coating with PS, the substrate color changed to a lighter shade of blue under the optical microscope. Poly(methyl methacrylate) (PMMA, $M_W \sim 120,000$, Sigma-Aldrich) was evaluated as a protective layer for reduced graphene oxide deposited on bare SiO$_2$. A PMMA solution of 0.2 wt.% in toluene was spin-coated onto substrates at 3000 RPM to yield a ~6 nm thick film [154]. No color change of the substrate was observed.

4.3.2. DPN Masking

Patterning of MHA masks and imaging of graphene flakes under the 10-nm Au film proceeded similarly to the method described in Section 3.3.3 for SWNTs. The major difference was the difficulty in discerning a single flake under the Au film due to low contrast in the LFM and error images. It was easier to look for the attached multilayer graphene and then compare the scanned image to its optical counterpart to estimate the location of single-layer graphene.

4.3.3. Defining Monolayer Graphene

Once the single-layer graphene was masked by DPN of MHA, the substrate was exposed to a ferric nitrate/thiourea etch (reagent volume 3 mL) for ~4 min. at 100
RPM (see Section 3.3.4 for details on preparing this etchant) to expose unmasked multilayer graphene. The substrate was then etched with O$_2$ plasma at 0.4 mbar, 80 W for 4 min. to eliminate the multilayer graphene and immersed in the Au etchant to reveal the monolayer graphene flake. It should be noted that these O$_2$ plasma conditions differ from those reported in literature [150] (~65 W for 7-20 s), which did not result in complete removal of multilayer graphene in our studies. We hypothesize that this discrepancy is due to differences between the O$_2$ plasma etchers.

### 4.3.4. Parylene-C Masking

Parylene-C shadow masks were used to pattern the larger Au electrodes (channel length at least 5 µm) on the substrate. Alignment of the channels in the parylene-C masks to the graphene was challenging. A particular mask can undergo a maximum of 6 attempts before its surface is fouled and it no longer laminates to the substrate. Securing the mask to two micromanipulators for ease of alignment did not work due to the flexible nature of the mask, making it sag when lowered towards the substrate. Instead, a manual method was developed (Figure 4.1) that entailed securing one end of the mask with a tweezer and slowly lowering it to the substrate under 10 X magnification in an optical microscope. The portion of the substrate farther from the graphene flake was temporarily secured to the microscope stage using double-sided tape so that repeated lifting and shifting of the mask did not disturb the substrate location. The limited working area under the microscope lens and the requirement of steady hands makes this setup nonideal. However, after practicing, 20 µm channels could be reliably aligned to graphene (location extrapolated from alignment markers...
on the substrate, see Figure 4.4) and 5-10 µm channels could be aligned after several slight adjustments to mask placement. Once alignment was verified through the measurement software of the microscope, a sticker backing was used to apply fingertip pressure on the mask for lamination. Care was taken not to disturb the mask during immobilization on a stage for thermal evaporation of Au (25 nm for Route 1 and 35 nm for Route 2, see Section 4.5). Graphene device characterization with AFM and electrical testing followed the methods discussed in Section 3.3.5 for SWNTs.

### 4.4. First DPN Step: Isolation of Monolayer Graphene

To facilitate contact to graphene flakes, DPN was used to isolate relatively large regions of monolayer graphene. These single-layer regions were identified under the optical microscope and matched to the AFM image of the flake under the Au thin film (Figure 4.2). The area to be masked by DPN of MHA was then designed, taking into account the inherent offset of the patterning process (discussed in Section 3.3.3). This offset was not as critical to device yield as in the case of SWNTs due to the larger room for error in isolating an arbitrary area of monolayer graphene.

![Figure 4.2. (a) Optical image of graphene flake before Au deposition. (b) LFM image of flake under 10 nm of Au. (c) Registration of MHA mask on the monolayer region. Grid pitch is 1 µm.](image)
The results of subsequent MHA masking, O\textsubscript{2} plasma etching of exposed multilayer graphene, and Au etching to reveal the monolayer flake are shown in Figure 4.3. In this particular sample, some of the multilayer graphene was masked as seen in the darker lower part of the flake. This overmasking is not a problem because the next step of patterning electrical contacts can be done over the multilayer region. It is important to note that the graphene flake remains in the same location on the substrate after multiple solution processing steps (two Au etches and rinsing steps).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4-3}
\caption{MHA-masked monolayer graphene (pink) after Au etching (a), O\textsubscript{2} plasma etching of exposed graphene layers (b), and Au etching to reveal the protected flake within the dotted black rectangle (c). The pairs of blue squares are alignment markers, each square being 5 µm on a side.}
\end{figure}

4.5. **Second DPN Step: Fabrication of Electrical Contacts**

For making contact to monolayer graphene flakes, another 10-nm Au film was deposited on the flake and one of two routes was taken: 1) parylene-C mask alignment to the flake (Figure 4.4a), followed by Au deposition and DPN masking of electrical contacts (similar to the steps in the SWNT study) or 2) DPN masking of electrical contacts, followed by Au etching and alignment of parylene-C masks to the MHA-masked contacts (Figure 4.4c). The benefits and disadvantages of each of these routes are discussed below.
In the first route, it was found that the thickness of Au deposited through the parylene-C masks was limited to below 25 nm. Any thicker Au films delaminated under Au etching after a few minutes. This effect is presumably due to the lack of an adhesion layer between the Au film and the SiO$_2$ substrate, allowing for the mechanical stress of flow to peel off relatively high aspect-ratio Au patterns. This limitation was not present in the SWNT system due to the amino-silane functionalized SiO$_2$, where the amine groups can bind to Au. Therefore, it is possible to circumvent this Au thickness limitation by treating the substrate with an amino-silane after the O$_2$ plasma step. Regardless, the first fabrication route still leaves the unmasked Au electrodes vulnerable to degradation during the Au etching step to define the graphene device. Figure 4.4b shows a device in which the larger Au electrodes are almost completely etched away.

To prevent degradation of these electrodes, a second fabrication route was developed in which the Au etching to define the graphene device is done before the larger Au contact pads are deposited. This second route has the advantage of not exposing the larger Au contacts to etching, thereby enabling the contacts to be an arbitrary thickness greater than 25 nm and ensuring their integrity (Figure 4.4d). Another advantage is enabling longer Au etching times to eliminate unmasked Au residue since MHA-masked Au is very robust under several minutes of extra etching. A disadvantage, however, is decreased flexibility in placement of the parylene-C mask (smaller margin for error) since the directionality of the MHA-masked contacts is already defined.
4.6. Electrical Characterization of Monolayer Graphene Devices

A representative graphene device fabricated via the first route described in the previous section is shown in Figure 4.5 along with its $I-V$ characteristics. There is residual Au on the substrate due to shorter etching times so as not to degrade the larger, unprotected Au contacts. Moreover, DPN overmasked into the SiO$_2$ region to the left of the monolayer graphene, as can be seen in the form of a faint residual feature in the AFM image (Figure 4.5a). This residue is suspected to consist of Au nanoparticles and is discussed in more detail in Section 4.7.

The field-effect cannot be observed due to the low range of applied $V_G$ and the outlier points are due to the limit of instrument sensitivity to such low source-drain voltages (Figure 4.5b). Nevertheless, the calculated resistivity of this graphene device is $4.6 \ \text{k\Omega}$ (via the scaling of measured resistance of $\sim31 \ \text{k\Omega}$ with W/L of the device for
$W = 885 \text{ nm and } L = 6 \mu\text{m}$), which is below the theoretical and experimentally verified $\rho_{\text{max}}$ of 6.5 kΩ at the expected charge neutrality point (Dirac point, $V_G = 0$) [155]. This lower resistivity value suggests that the Dirac point has shifted due to the graphene being doped. It has been shown that graphene exhibits p-type doping behavior in ambient conditions due to physisorbed ambient impurities such as water [3] and oxygen [156]. Additionally, Au has been shown to have a hole-doping effect on graphene [157]; however, it remains inconclusive whether such an effect is being caused by the residual nanoparticles on our graphene devices.

Figure 4.5. (a) AFM topography image of DPN-generated graphene device. (b) Corresponding output curves for sweeping $V_G$ from -0.5 to 0.5 V.

In addition to the NP residue, some graphene devices also contained cracks after processing. The AFM image in Figure 4.6 shows such damage to a device fabricated without MHA-masked electrodes by careful alignment of the 5-µm channel parylene-C mask to an isolated monolayer graphene flake. Furthermore, the overmasked region can be discerned by the residual NPs on the surrounding SiO$_2$. The corresponding output curves yield resistivity values (18 to 23 kΩ for $W = 1.4 \mu\text{m}, L = 3.6 \mu\text{m}$) that
are higher than the device in Figure 4.5, which does not contain any cracks; the smaller flake area may be less than the average area for which one macroscopic fracture forms. Since the resistivity increases past $V_G = 0$ to $\sim 9 \, \Omega$ at $V_G = 15 \, V$, the Dirac point is shifted at least $+15 \, V$, indicating that there is indeed p-type doping in the graphene.

Figure 4.6. (Left) AFM topography image of graphene device fabricated by direct alignment of parylene-C shadow mask to DPN-defined monolayer flake. (Right) Corresponding output curves sweeping from $V_G = -20$ to $15 \, V$.

4.7. **Damage to Graphene During Processing**

A series of troubleshooting experiments were conducted to determine the cause of these residual NPs and cracking in the graphene. The state of the graphene flakes was assessed after each processing step.

4.7.1. **Au Deposition and Etching**

To test whether there was any damage to the graphene after deposition of the 10 nm Au film and subsequent etching, an exfoliated graphene substrate was subject to the aforementioned processing steps (without any DPN patterning). The results are shown in Figure 4.7, where cracks in the large flake and shifts in the narrow flakes are
observed. These cracks may be due to high energy Au atoms impinging on graphene surface and intercalating between the monolayer graphene and the underlying SiO₂ substrate, decoupling the graphene from the substrate [157]. This intercalation effect may serve to further weaken the graphene at certain defect sites, which have been shown to preferentially adsorb Au [158], thereby making the flake more susceptible to fracture during wet etching. There is a higher frequency of damage to larger flakes (cracks are absent from the narrow flakes); this effect may be due to the incomplete decoupling of such large areas from the substrate surface, which leads to strain in the graphene as the decoupled parts shift and the other parts stick to the substrate during the wet Au etch. The decoupling of the graphene from the substrate is further supported by the shifting of the narrower graphene flakes on substrate during Au etching (Figure 4.7c).

Figure 4.7. AFM images of graphene flakes before (a) and after (b,c) Au deposition and etching.

To verify that this effect is due to the Au deposition and not just the agitation during the wet etching step, another exfoliated graphene substrate was only exposed to the etching step. Figure 4.8 shows that no cracks were observed after this step; therefore, the combined Au deposition and subsequent etching steps cause fracturing
in graphene. Similar cracks have been observed in the literature with transfer printing of graphene using a Au film [159].

Figure 4.8. AFM topography images of exfoliated graphene on SiO\(_2\) before (left) and after (right) exposure to wet Au etchant.

4.7.2. O\(_2\) Plasma Treatment of Au Film

Although the cause of the macroscopic cracks was determined, the cause of the NP residue still remained unsolved. A literature search for AFM images of graphene devices turned up only one set of papers [148, 160]; most graphene devices are reported in the form of SEM images in the literature. These AFM images (Figure 4.9) reveal that the graphene is not pristine and indeed contains some NP residue. However, neither the cause nor the consequences of such surface contamination are discussed.
Further Au etching of the graphene flakes in this study revealed some abatement of the NP residue (Figure 4.10) suggesting that the NPs consist of Au. In order to pinpoint the source of this NP residue, a series of control experiments were performed on Au thin films deposited onto bare SiO$_2$ and exposed to O$_2$ plasma. Optical microscopy showed that the 10-nm Au films changed color from pink (Figure 4.11a) to blue (Figure 4.11b) upon O$_2$ plasma treatment, an effect that has been reported previously and attributed to oxidation of the Au; however, this color change is not completely reversible, as it should be after this unstable Au oxide reverts to metallic Au at room temperature after one day or faster upon heating of the Au film [161].
Figure 4.10. AFM topography images of a graphene flake exposed to additional Au etching for 8 (top) and 13 (bottom) min.

Figure 4.11. Optical images of Au film on SiO$_2$ before (a) and after (b) O$_2$ plasma treatment. AFM images of SiO$_2$ after etching of Au film without (c) and with (d) O$_2$ plasma treatment.

AFM reveals that even after prolonged Au etching (13 min.) and solvent rinsing, the NP residue (average height of 2 nm) still remains (Figure 4.11d). This residue is not seen after etching Au films not exposed to O$_2$ plasma (Figure 4.11c) or on bare SiO$_2$ exposed to O$_2$ plasma. Therefore, it is the O$_2$ plasma treatment of Au that causes this NP residue. If the NPs were just gold oxide, they should be reduced by the HCl in the Au etchant, heating to $\sim$160 °C, or submersing for 1 hr in a 0.1 M ethanolic solution of triphenylphosphine [161]. Therefore, the NPs are probably not gold oxide. However, even after Au etching of the substrate in Figure 4.11d one week later, the
nanoparticle residue remained on the surface. Neither mechanical swabbing nor sonication in various solvents (toluene, acetone, or isopropanol) removes this NP residue. We hypothesize that this residue is composed of Au NPs complexed with carbonaceous contaminants from the O₂ plasma chamber that shields the Au NPs from etching.

4.8. Mitigation of Nanoparticle Residue

In an attempt to reduce or eliminate this NP residue, a sacrificial polymer layer (PS) was sandwiched between the graphene and Au thin film. This layer served two functions: 1) to reduce strain on graphene during Au deposition and etching by preventing the intercalation of Au atoms and 2) to facilitate removal of residual NPs after etching. Results indicate that the first function may be satisfied due to the absence of cracks in the graphene after processing; however NP residue still remains on the surface.

Figure 4.12a,b shows that the reduced graphene oxide surface looks the same (note the absence of cracks) before and after spin-coating of low molecular weight PS, Au deposition and subsequent etching, and toluene rinsing. This result indicates that the PS film is protective and also rinses off cleanly as a sacrificial layer should. However, once the O₂ plasma step was introduced, the NP residue appeared on the substrate surface after removal of Au film and toluene rinsing (Figure 4.12c). Even after increasing the thickness of the protective film to > 15 nm using higher concentrations of PS solution, the NP residue remained.
Figure 4.12. AFM topography images of reduced graphene oxide on SiO$_2$ before (a) and after spin-coating low molecular weight PS, deposition and subsequent etch of Au film, and toluene rinsing (b). (c) The reduced graphene oxide substrate after an additional O$_2$ plasma step before the Au etching.

A higher molecular weight PS film was then used; however, the resultant polymer film was more difficult to remove from the graphene surface. Figure 4.13a shows that the previous condition of a 10-20 min. toluene rinse was insufficient; the film was only dissolved after 1 hr in toluene (Figure 4.13b). Again, no cracks are evident in the graphene, yet the NP residue remains.

Figure 4.13. High molecular weight PS film on graphene (a,b) and PMMA film on SiO$_2$ after Au film exposed to O$_2$ plasma (c).

PMMA was then evaluated for its ability to prevent NP residue formation by O$_2$ plasma exposure of Au films deposited onto SiO$_2$ coated with PMMA. After Au etching and sonication in acetone for 10 min., the NP residue was still present (Figure 4.13c). Further experiments revealed that the NP residue appears even for thicker Au films (40 nm) and shorter O$_2$ plasma exposure time (1 min.) and lower power (50 W).
It should be noted that although UV-ozone would be a less harsh method for multilayer graphene removal potentially avoiding this NP residue formation, it would take several hours and is therefore not practical.

4.9. **DPN of Electrical Contacts to Reduced Graphene Oxide**

To avoid masking of the monolayer graphene (and hence exposure to O\textsubscript{2} plasma) that leads to the NP residue, preliminary experiments were conducted with monolayer nanoplatelets (~300-500 nm in diameter) of reduced graphene oxide (rGO). The small dimensions of these nanoplatelets made the DPN process difficult due to the inherent offset of ~500 nm from a designed pattern. Moreover, individual monolayer nanoplatelets were difficult to see under the 10 nm Au film (Figure 4.14a); only multilayer flakes show up clearly. Therefore, most patterns were placed randomly on the channel region, with designed widths of 1-2 \(\mu\)m and gaps of < 300 nm to increase the probability of contacting at least one nanoplatelet. These gap sizes approach the reliability limit for patterning of DPN gaps, and therefore only 14% of the patterned devices did not short.

Figure 4.14 shows a nanoplatelet device with a channel length of 180 nm. The high resolution phase image clearly shows at least one nanoplatelet being contacted; however, electrical testing results were insulating, even with applied \(V_G\) bias up to 100 V. XPS verified that this sample contains hydrazine-reduced graphene oxide (Figure 4.14), and so should be conductive. The device was still insulating even after annealing at 290 C for 20 min and exposure to GoldEnhance solution for 10 min., which resulted in doubling of the Au height. Figure 4.14f shows a similar case of
insulating electrical behavior that occurred with one exfoliated graphene device that also had a small contact area (due to DPN offset in the +y direction).

Figure 4.14. (a) LFM image of rGO nanoplatelets under 10 nm of Au. (b) AFM topography image of DPN-patterned rGO nanoplatelet device. (c) XPS spectrum of rGO substrate. (d) Optical image of rGO device in (b). (e) AFM phase image of channel region in rGO device. (f) AFM phase image of DPN-patterned top contact to an isolated monolayer of exfoliated graphene.

Besides the difficulties in registration of contacts to these nanoplatelets, the Au films deposited on these substrates are rougher than on the exfoliated graphene substrates, possibly due to debris from spin casting of the reduced graphene oxide. This roughness may also have caused the Au films to etch at a faster rate (2 X faster than seen with Au on SWNT or exfoliated graphene substrates) due to etchant seeping into nanoscale cracks in the film. This substrate effect on the Au etching rate has been observed in other experiments where a 10-nm Au film on bare SiO₂ took 4 min. to etch, whereas the same Au film on SiO₂ functionalized with a hydrophobic SAM took
6 min. The discrepancy in etch rate may be due to the different morphology of the Au thin film that forms during thermal evaporation onto the substrates. The presence of a SAM may smooth the SiO$_2$ surface, thereby promoting a more closely packed Au film that requires a longer etching time.

**4.10. Conclusions**

DPN did not perform better than EBL for making contact to exfoliated graphene flakes, due to fracture during Au deposition and etching to define monolayer graphene for devices and also a hole-doping effect from the processing. The fracture problem was not observed in the SWNT system, presumably because carbon nanotubes have a much smaller surface area and are more rigid than planar graphene, therefore less susceptible to deformation [162]. Moreover, masking monolayer graphene with DPN-patterned Au during O$_2$ plasma treatment results in residual NP contamination on the regions of the substrate formerly masked with Au. This residue could not be eliminated through various post-processing steps or even with the use of polymer sacrificial layers protecting the underlying graphene, which seemed to at least prevent fracture. Slight decrease in residue after prolonged Au etching leads us to hypothesize that this residue consists of a carbonaceous shell surrounding Au NPs. This hypothesis is consistent with the p-type doping observed in the resultant graphene devices. Therefore, this DPN fabrication method does not seem amenable for conducting fundamental studies on graphene; however, these composite structures may be of interest for new catalytic and optoelectronic materials [163]. Furthermore, if the residue were not an issue, perhaps there is merit in using DPN to fabricate
nanoribbons and other more complex nanostructures of graphene since these structures are difficult to make using EBL and the frequency of fracture for these nanostructures is much lower than for the larger, micron-sized flakes used in this study.
5. Indirect Patterning of Electrical Contacts to Organic Semiconducting Grains

Section 5.1 provides the motivation for forming electrical contacts to organic semiconducting (OSC) grains. Sections 5.2 and 5.3 discuss the experimental design and preliminary results, respectively. Alternative fabrication routes to address some of the issues with direct translation of DPN-patterning are presented in Section 5.4.

5.1. Background

Fundamental charge transport studies of organic semiconductors have been performed on organic single-crystal FETs [164, 165], which provide insight into the optically and electrically anisotropic characteristics of these materials. Anisotropic mobility could be useful in engineering logic circuits or pixel-switching elements in displays so as to isolate neighboring components and reduce the cross-talk effect [166]. Fabrication of these organic single-crystal FETs is challenging since the surface of organic crystals can be damaged much more easily than that of their inorganic counterparts, and organic materials are usually incompatible with conventional microelectronic processing techniques such as photolithography, sputtering, etc. [167]. Therefore, these devices are usually fabricated by manual selection and placing of individual crystals – a tedious process for producing devices at high density and with reasonable throughput [168]. The handpicking process also can easily introduce contamination and crystal damage, which often results in lower performance of the device [169]. Furthermore, it is very difficult to fabricate devices using very small organic crystals (sub-micron in size) using this handpicking process.
The mild processing conditions of DPN (aqueous solvents, ambient conditions) may facilitate fabrication of devices containing sub-micron single-crystals or grains for fundamental studies of their material properties. Single-grain measurements on sexithiophene (6T) have been conducted using a conducting-probe AFM; however, the selection of grains for study depended on contact to an existing electrode and the contact resistance was found to dominate device performance (Figure 5.1). The 6T grains ranged from 1 to 6 molecules (~2–14 nm) in thickness, 1–2 µm in length and width, and were deposited by thermal evaporation onto SiO₂ substrates previously patterned with 200 nm wide Au wires. Au-coated AFM probes were used to image the substrates in air to identify individual 6T grains which grew in contact with a wire. The same probes were used to record the $I-V$ characteristics of single grains. The grain resistivity is approximately 100 Ohm-cm, which is much smaller than reported values ($10^{12}$ Ohm-cm) for single crystals of 6T in vacuum [170].

![Figure 5.1. CP-AFM measurement of a sexithiophene single grain. Reproduced from Ref. [170]. Copyright American Vacuum Society.](image)
5.2. **Experimental Design**

The preliminary experiments on DPN-masking of electrical contacts to single OSC grains followed the same processing steps as for the SWNT system (see Section 3.2). Submonolayers of organic grains were evaporated onto 300-nm SiO$_2$/Si substrates containing microscale electrodes, then a 10-nm layer of Au was evaporated and DPN of MHA was used to mask electrical contacts to the grains. The unmasked Au was then etched with the ferri/ferrocyanide system to reveal the OSC devices.

5.3. **Preliminary Results and Conclusions with Various Organic Semiconductors**

5.3.1. **Thioanthracene**

DPN masking of contacts was attempted first on thioanthracene grains (deposition thickness: 40 nm) due to their relatively large size (> 1 µm in width) to facilitate registration to the grain. However, the grains were too rough for adequate diffusion of MHA on the Au film. Figure 5.2 shows the limited diffusion of MHA as evidenced by the lack of contrast in the LFM image.

![AFM image of thioanthracene grains on SiO$_2$. Scan size 5 µm. (Inset) LFM image of MHA pattern on a single grain.](image)

Figure 5.2.
5.3.2. Pentacene

A smoother grain of pentacene (deposition thickness: 3 nm) was chosen next for DPN masking; however, the grains delaminated after 5 minutes in the ferri/ferrocyanide etchant under constant stirring (Figure 5.3). Therefore, the next choice of OSC was C12FTTF due to its water stability [171].

![AFM images of pentacene grains before (a) and after (b) exposure to Au etchant.](image)

Figure 5.3. AFM images of pentacene grains before (a) and after (b) exposure to Au etchant.

5.3.3. C12-FTTF

5.3.3.1. Effect of Processing on Electrical Performance

C12FTTF thin-film devices were exposed to ferri/ferrocyanide etchant and evaluated for any damage. Figure 5.4 shows crack formation in the thin film, which corresponds to an order of magnitude decrease in C12FTTF mobility (Figure 5.5). However, since the cracks were microscopic, we decided to continue with patterning of contacts to C12FTTF grains.
Figure 5.4. (Left) Optical image of C12FTTF thin-film device after exposure to ferri/ferrocyanide etchant. (Right) AFM image of resultant damage to the C12FTTF film.

Figure 5.5. Transfer characteristics of C12FTTF thin-film device before (left) and after (right) exposure to ferri/ferrocyanide etchant.

5.3.3.2. DPN of Electrical Contacts

C12FTTF was evaporated onto SiO₂ (deposition thickness: 1.5 nm) at various deposition temperatures to tune the grain size, with higher substrate temperatures corresponding to larger grain sizes of 5-15 µm (Figure 5.6). DPN masking was then attempted on the largest grains. The optical image of the device after 9 min. of Au
etching revealed an interesting phenomenon of being able to see the C12FTTF grains, presumably due to Au embedded in the grains as seen in the AFM image (Figure 5.7). This observation may be useful for rapid screening of various grain morphologies under different deposition conditions (temperature, rate, etc.). Electrical testing of the resultant device revealed that the residual Au forms a conductive path between the MHA-masked contacts. After further etching, the organic grain seems to have dissolved, leaving only nanoparticles encapsulated by an organic shell (Figure 5.8). XPS analysis revealed that these nanoparticles are most likely residual Au (Figure 5.9). The determent of Au etching by an organic shell was observed also in the graphene device study. This observation led us to postulate alternative, non-destructive methods for Au film deposition onto OSC grains.

Figure 5.6. AFM images of C12FTTF grains deposited at 0.1 Å/s on SiO₂ at 70 °C (a), 110 °C (b), and 146 °C (c).
Figure 5.7. (a) AFM image of MHA-masked contacts to a C12FTTF grain. Optical (b) and AFM (c) images of device after Au etching.

Figure 5.8. AFM images of Au on C12FTTF grains after etching in ferri/ferrocyanide for 18 min. (left) and 21 min. (right).
Figure 5.9. XPS spectra after Au etch of 10 nm Au films on SiO$_2$ (top) and a submonolayer of C12FTTF (bottom). Note the absence of an Fe peak (no Fe doping) and the higher Au concentration on the C12FTTF sample.

### 5.4. Alternative Fabrication Schemes

Since the direct deposition on Au onto OSC grains is not a viable method due to the destructive penetration of Au through the thin organic layer, we propose two alternative methods for DPN of electrical contacts (Figure 5.10). The first involves PDMS-transfer of the Au film onto OSC grains. A fluorosilane on the PDMS-side of the Au film promotes detachment of film onto the OSC and SiO$_2$ surface. Au transfer can be further assisted by functionalizing the Au surface with a Ti adhesion layer or mercaptosilane. A possible issue with this method is contamination of the Au with PDMS residue; however, that may be eliminated with UV-ozone cleaning. Another
issue may be conformal contact of the Au film to the OSC grain to allow for targeted patterning of contacts.

Figure 5.10. Schematic of two alternative fabrication routes for DPN of electrical contacts to OSC grains.

The second scheme involves SiO₂-templating of OSC grains evaporated on a Au film. The SiO₂ surface is treated with a fluorosilane to enable the release of the Au film [172], which is then bonded to a PDMS dielectric functionalized with mercaptosilane (or bonded using epoxy at borders). Conformal contact of the Au film to the OSC grain is also an issue in this case. To circumvent these multistep processes, a setup allowing “cold gold” evaporation via a cooled stage (77 K) and Ar purging may be used to prevent Au penetration into the OSC grains [173, 174].
6. Conclusions

6.1. Project Summary

We have successfully demonstrated DPN of electrical contacts to 1D and 2D nanostructures of SWNTs and graphene, respectively. The performance of both types of devices was benchmarked to those fabricated \textit{via} EBL, being within an order of magnitude in figures of merit such as field-effect mobility, transconductance, and resistance. Damage to graphene flakes was visible during the device fabrication process in the form of fracture and surface contamination. The former issue seems to be mitigated by a sacrificial polymer layer, and the latter issue can be observed in other EBL-fabricated devices reported in the literature. These results motivate further investigation into the possible effects of surface contamination on graphene measurements.

Direct patterning of Au NPs was also demonstrated, albeit on limited surface chemistries (hydrophilic or thiol-functionalized). Long-range patterning was achieved only after a serial ink concentrating process was developed. Furthermore, the relative humidity could be controlled to tune feature size and amount of deposition. The direct write of Au NPs is not of a sufficient amount for electrical contact applications; however, this method may be used to precisely deposit Au NPs as catalyst particles for the bottom-up assembly of nanowire devices.
6.2. **Future Applications**

Near-term, direct applications of the DPN patterning of electrical contacts include contacting new carbon nanotube structures, such as the ones shown in Figure 6.1. Y-shaped carbon nanotubes have been shown to be gated through one of the branches [175], and the conductance has been shown to be modulated along a carbon nanotube coil [176]. DPN enables rapid prototyping of devices to screen and study these new nanostructures.

![Image of Y-shaped carbon nanotube and carbon nanotube coil](image)

**Figure 6.1.** (Left) AFM image of a Y-shaped carbon nanotube. Reproduced from Ref. [175]. Copyright American Chemical Society. (Right) SEM image of a carbon nanotube coil. Reproduced from Ref. [176]. Copyright Springer.

Longer term development of this technique includes extension to 3D systems of OSC grains. Moreover, cleaner imaging of nanostructures for registration of MHA masks can be obtained using a multipen probe with a microfluidic inkwell array (Figure 6.2) to keep the reader pen ink-free. Massively parallel electrode fabrication can also be achieved with a 2D nano PrintArray. However, this type of patterning does not allow for directed targeting of nanostructures for device fabrication. Parallel electrode fabrication would be useful for statistical studies on nanostructure properties, with higher yield of devices when the nanostructure spacing and alignment can be controlled on the substrate.
6.3. **General Caveats for Dip-Pen Nanolithography**

The following is a listing of various aspects of the NSCIPTOR instrument that may cause potential problems during experiments:

1. Internet (LAN) must be disabled during DPN use; otherwise, interference of communication between the DPN controller and the desktop computer may interrupt patterning.

2. When imaging in AC mode, the cantilever frequency should be tuned manually to prevent instrument crash. If the drive amplitude is greater than 2 or the setpoint is less than an absolute value of 0.3 V then restart the instrument and repeat the frequency tuning to within typical ranges of < 1 and absolute value of 0.5 V, respectively.

3. It is best not to interrupt any processes and perform one operation at a time to avoid instrument crash. Lithography can be stopped only at the end of patterning each continuous feature, so it is best not to make individual elements too large in InkCAD.
4. The InkCAL software may underestimate transport rate of MHA. It is best to calibrate the transport rate using patterns of similar size to the desired feature.

5. If initial scanning with an MHA coated tip seems blurry or there is streaking across images, there may be deposition of ink during scanning. Scan a large area (> 10 µm scan size) rapidly (> 5 Hz) to relieve the tip of excess ink.

6. It is faster to ramp up the humidity in the chamber using a beaker of boiling water rather than the built-in nebulizer.

7. DPN image registration issue does not seem to be due to image shifting at higher scan speeds since these speeds cause the uploaded forward images to shift to the left, which is exactly the opposite of the observed shift in resultant pattern. Shifts are mainly observed in the fast-scan (x) direction. The slow scan (y-direction) shift is negligible and independent of scan speed. The cause of such shifting is presently unknown; thermal drift (0.05 nm/s) can only account for offsets an order of magnitude lower than what has been observed [177].

8. If better alignment to nanostructures is desired, an alignment procedure (filed under: layer-by-layer alignment) with a DPN-patterned marker within patterning range of the nanostructure can be used to get within ~200 nm.

9. Contact mode probes need to be stored under desiccant in the fridge, otherwise contamination from polymer casing and ambient environment causes cantilever to bend, thereby preventing an adequate laser signal for imaging. Also, residue on tips prevents proper inking, resulting in sparse and irregular
patterns. UVO-cleaning old tips for 20 min. restored them to the original condition.

10. If there is trouble with the tip approach, most likely the cantilever is bent or the motor has reached its limit (around Z > 1750 µm). If the latter case, either reset the limit by raising all Z motors to the zero position or physically raise the stage (using extra pucks).
7. References


