ATMOSPHERIC-PRESSURE *in situ* PLASMA REDUCTION AND PATTERNING OF METAL-ION CONTAINING POLYMERS

by

SOUVIK GHOSH

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Department of Chemical and Biomolecular Engineering

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CASE WESTERN RESERVE UNIVERSITY
SCHOOL OF GRADUATE STUDIES

We hereby approve the dissertation of

Souvik Ghosh

candidate for the degree of Doctor of Philosophy. *

Committee Chair
R. Mohan Sankaran

Committee Member
Daniel J. Lacks

Committee Member
Rohan Akolkar

Committee Member
Christian A. Zorman

Committee Member
Philip X-L. Feng

Date of defense
January 31st, 2017

*We also certify that written approval has been obtained for any proprietary material contained therein.
Dedicated to my mom and dad, whose love and support helped me complete this adventure…
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Souvik Ghosh
Atmospheric-Pressure *In Situ* Plasma Reduction And Patterning Of Metal-Ion Containing Polymers

Abstract

by

Souvik Ghosh

In this dissertation, we are describing a plasma based approach to fabricate electrical conductors on the surface of thin polymer films. We incorporated a direct-write approach derived from additive manufacturing techniques that minimizes wastage; and a post-patterning thin film removal and transfer protocol derived from subtractive manufacturing techniques. Using such a hybrid protocol, we made electrically conducting patterns embedded at the surface of polymeric thin films or deposited on affordable non-rigid substrates such as paper without incorporating the complexities of making a stabilized nanoparticle ink or high temperature annealing.

In this first section of this dissertation, we describe the fabrication of thin films of polyacrylic acid after mixing silver nitrate in solution and blade casting them as thin films. The DC and AC argon microplasma based direct-write patterning was performed after mounting these films on a programmable x-y stage. Microplasma exposure lead to the formation of electrically conductive patterns of reduced and percolated silver nanoparticles. Further, by incorporating an elastomer as the support structure for the thin films enabled us to fabricate stretchable electrical conductors. We discovered an electrodiffusion phenomena whereby the plasma can drive the silver ions from the bulk of the film to the surface leading to percolation of reduced silver nanostructures.
In the later part of the dissertation, we describe our efforts to understand the plasma reduction process by exposing these thin films to a controlled atmospheric-pressure and low-pressure plasma. It was found that photons from the plasma alone cannot reduce the nanoparticles. Instead, it was found that nanoparticle agglomeration and percolation depend on both, the properties of the thin film such as concentration and thickness, and the plasma operating parameters such as pressure, exposure time, and period and duty cycle of the driving pulse. We conclude that the harmonious effect of all these parameters contribute to controlling the particle size, number density and distribution of the nanoparticles at the surface of the polymer.
Chapter 1

Introduction and Motivation

1.1. Introduction

Fabrication of flexible, patterned, electrically conductive features as a contact or interconnect is critical for a wide range of technological applications ranging from electronics to energy to medicine.[1,2,3,4,5] Traditionally, solid sources of metals either in the form of a powder or foil are either sputtered or evaporated as a thin film on top of a substrate and then selectively removed by a combination of photolithography and etching (wet or dry). This is generally known as subtractive since a part of the metal is removed or subtracted from its final form to produce the desired pattern. Subtractive approaches remain the state-of-the-art for many applications because of high pattern fidelity, high and reproducible electrical conductivity close to the bulk metal, and high purity. However, there are several drawbacks including costs associated with the capital equipment and operating in vacuum, low throughput, and materials wastage. In addition, as we will discuss, the integration of metals and polymers is an obstacle since some polymers and solvents may not be compatible with vacuum and combining the metal and polymer separately can lead to interfacial issues.

More recently, additive approaches or additive manufacturing has emerged which refers to the selective fabrication of metal patterns, also referred to as direct write. Examples include ink-jet printing,[6,7] aerosol-jet printing [8,9] and electrohydrodynamic-jet printing.[10,11] Additive approaches are usually carried out in the ambient, making it easier to process polymers and integrate with roll-to-roll processing for large-scale manufacturing. A common feature of these approaches is the need for inks, typically composed or organic-ligand stabilized dispersions of
metal nanoparticles, which can be expensive, unstable, and limited to certain metals. Further, high temperature sintering that is required for removal of the organic stabilizers and sinter the nanoparticles limits the applicability to mostly high temperature compatible substrates.\[12,13\] A schematic summarizing the main techniques used for subtractive and additive manufacturing is shown in Figure 1.1(a) and 1.1(b).
Figure 1.1. Simplified schematics of (a) subtractive methods such as sputtering and thermal evaporation, (b) additive methods such as inkjet printing followed by sintering and (c) in situ fabrication methods such as scanning laser and electron beam direct-write and AFM nanopatterning.

Research has slowly emerged which combines subtractive and additive approaches and is characterized by the in situ activation or conversion of metal precursors in polymer substrates. Figure 1.1(c) is a simplified representation of three in situ methods to fabricate electrically conducting patterns on non-traditional (e.g., Si, Ge) substrates. The stimulus for the activation/conversion can be photons (e.g., UV light or laser), heat or electrical current, chemical reagents, electron beam, or plasmas. These approaches are detailed below.

1.1.1. UV and laser photoreduction

Photoreduction is a very versatile technique that is compatible for implementation with solid, liquid and gas phase precursors.[14] In particular, photo-induced reduction and growth of thin patterned films and selective laser sintering for 3D growth has been one of the most promising techniques for direct-write manufacturing.[15] This methodology can efficiently combine the advantages of additive and subtractive manufacturing.[16] One of the early reports of laser-induced reduction of metal salts from thin films was reported by Gross et al., showing the reduction of Pd from Pd acetate thin films in a one-step direct-write process.[17] In a later study, Stellacci et al. translated this process to direct-write 3D geometries of Ag.[18] Similar results were also reported by Tanaka et al. with Ag and Au.[19] Multiple mechanisms for the reduction have been proposed.[20,21,22,23,24,25] Among these, the most accepted model is that irradiating the metal-
polymer thin films with high energy photons give rise to localized heating, creating phonons. These phonons can splice the metal ions that are otherwise bound with the polymer and subsequently reduce, nucleate and sinter them as nanoparticles. Under optimal conditions, the phonons can also splice the polymer chains into smaller carbonaceous compounds. The excess heat is then dissipated by refraction through sub-wavelength nanostructures.[26] Moreover, because the laser-induced temperature field is localized to a small area, the technique is compatible with flexible polymer substrates.[27,28] Laser reduction and sintering is highly sensitive to ambient conditions such as humidity and temperature, and is, therefore, usually carried out in controlled atmosphere conditions. With proper tuning of the absorption coefficient of the precursor materials for the laser wavelength and coupling it with near-field optics, laser based direct-write approaches can produce features close to the diffraction limit (~500 nm).[29] Other optical methods of reduction and sintering of metal ions with stimuli such as UV and flash sintering have also been reported.[30,31] Both of these involve heat and phonon energy transfer, effectively accelerating the reduction rate and growth of nanoparticles.

1.1.2. Localized heating or electrical current induced reduction and patterning

An alternative to laser and UV induced phonon generation is to use an AFM tip to site-selectively heat the surface of a thin film. In one of the early works, Szoszkiewicz et al. used a heated AFM cantilever to hydrophilize the surface of a hydrophobic polymer at resolutions as high as <15 nm. [32] Sheehan and coworkers were later able to advance this process to create nano-sites of reduced graphene oxide (r-GO) and reduced graphene fluoride (r-GF) on a GO and GF substrates respectively using a heated probe tip.[33,34] For the most part, research on thermal, thermochemical, and biased tip based patterning has been limited to carbon and polymer functionalization and site-selective activation. [35,36,37,38,39,40] In a limited number of studies,
Maynor et al. and Li et al. were successful in inducing a substrate effect coupled with a heated or biased probe to reduce Au and Pt respectively.[41,42] More recently, Mirkin and coworkers used a similar technique to produce multimetallic alloy nanoparticles containing a combination of Ag, Au, Pt, Ni, Co, or Pd by depositing them from the liquid phase with local heated or current probes and then applying external heat to sinter and alloy them.[43,44] Their proposed mechanism suggests that the polymer stabilized metal ions diffuse through the polymer chains and reduce near the heated AFM tip. Scanning the heated AFM tip across the substrate can therefore create a well-controlled array of nanoparticles.

1.1.3. **Electron-beam (e-beam) reduction**

When a collimated beam of electrons impacts a surface containing metal ions, they get absorbed and can be reduced to electrically neutral atoms. Because of the advancements in electron beam (e-beam) technology, this method allows sub-10 nm features to be generated with a throughput ~1.5 min/cm².[45] Recently, e-beams have been used by multiple researchers for the synthesis of nanoparticles as summarized in a recent review by Gonzalez-Martinez et al.[46] Briefly, this technique locally reduces metal ions dispersed in a thin polymer film and by scanning, directly writes a pattern. After the metal ions are selectively reduced, the unreduced regions can be removed with an appropriate solvent.[47,48,49,50] E-beam direct-write on thin films containing metal salts, organometallic complexes, and metal-polymer thin films have all been reported in literature. In particular, this technique has been successful in producing patterns of different metals including Ag, Au, Pd, Pt and Zn [51,52,53,54] Since e-beam patterning is carried out in high vacuum, the reduction of metal ions is also accompanied by chain scission of the polymer which leads to insoluble carbonaceous residues. Therefore, after reduction, a high temperature sintering
of the reduced areas is usually required to produce percolated nanoparticles that are electrically conducting.[55,56,57,58]

1.1.4. Chemical reduction after patterning

Ink-jet printing is a state-of-the-art method for producing patterns of metal nanoparticles. However, nozzle clogging and shelf-life of inks consisting of nanoparticles limits the applicability of this process. In order to avoid these limitations, particle-free inks have been reported which must be post-reduced after depositing to produce nanoparticles. In one of the first reports, Walker et al. reported the synthesis of particle free reactive silver inks that could be reduced by heating the patterns after printing.[59] However, polymer substrates are susceptible to high temperatures. Alternatively, Wakuda et al. described a method to remove the organic stabilizers by dissolving them in alcohol.[60,61] In a later study, Magdassi and coworkers showed that the presence of a charge-neutralizing polymer on top of the active nanoparticle ink can reduce the resistivity of the printed Ag nanoparticles, achieving conductivity up to 20% of the bulk value.[62] More recently, reactive silver inks deposited using a ball-point pen were reduced at room temperature using a formaldehyde bath. [63] Chemical sintering and removal or organics to enable percolation of printed nanoparticles were demonstrated in multiple reports, with metals ranging from noble metals such as Ag and Au, to cheaper transition metals such as Cu and Ni;[64,65,66] all producing resistivities ~µΩ-cm. In general, this protocol either involves treatment of the printed components in a compatible chemical bath, solvent vapor to remove or dissolve out the organics or multiple deposition steps of the ink followed by a reducing agent to achieve high conductivities.[67,68]
1.2. Plasma reduction of metals on surfaces of metal-ion containing polymers

Plasmas are electrical discharges in gases containing ions, electrons, and other energetic species. Similar to e-beams, these species can interact with metal ions on a surface to reduce and form metal nanoparticles. In one of the early reports, Crowther showed that gold chloride, silver nitrate, and palladium acetate dispersed in a polymer and cast as a thin film can be reduced to the respective nanoparticles when exposed to a H$_2$ plasma.[69,70] In a separate report, Sawada et al. were able to reduce thin films of Cu$_2$O to Cu on treating it with a H$_2$ plasma.[71] The authors argued that hydrogen species (e.g. H$_2^*$ or H*) from the plasma react with the organics and the metal ions and subsequently reduce the metal ions and convert the carbon to hydrates. It was later shown by C. J. Liu and others that it is not necessary to use a H$_2$ plasma to reduce metal ions; inert gas plasmas such as Ar and He can also reduce metal ions to metal nanoparticles.[72,73,74] In separate studies, plasma reduction of several metal ions including Cu, Zn and Ni were demonstrated by several groups.[75,76,77,78,79,80,81,82,83] However, most of these studies usually relied on controlled atmospheric conditions to preserve the post-reaction oxidation state of the elements, making it hard to perform studies of the plasma reaction. In order to study the mechanics of the plasma reduction, Bromberg et al. showed that exposure of printed AgNO$_3$ tracks to a radio-frequency plasma can induce rapid reaction and sintering at the surface of the films.[84] In their study, the underlying layers remain unreduced due to skin effect, unless prolonged exposure at relatively high plasma power is applied.[85] Alternatively, high processing time was reported to affect the morphology of the substrate polymers and therefore is disadvantageous.[86] In the same study by Wunscher and coworkers, they also attempted to address this by using an atmospheric pressure plasma where the ion and electron energies are very low.[87] It was found that the reduction and sintering depended on ink formulation, primarily since the charged species
from the plasma remove the stabilizing polymer by chain scission. Due to the low energy of charged species, atmospheric-pressure remote plasmas are not ideal to induce chain scission.[88] This could be addressed only by either ramping up the plasma power or substrate temperature or both.[89] However, this limits the approach to thermally stable materials such as inorganic non-flexible substrates. In addition to these technological challenges, the mechanism of reduction remains an open question. Specifically, how the interaction of charged species from the plasma with metal ions leads to the formation of metal nanoparticles has not yet been revealed. The fundamental understanding of these phenomena can potentially be applicable to a wide array of applications such as surface modification,[90] biosensors,[91,92,93] actuators,[94] and RFID tags and antennas.[95,96]

This thesis presents a detailed study of plasma-based processes for the in situ fabrication of Ag nanoparticles in polymer thin films. Our primary goal was to produce electrically-conductive, flexible or stretchable patterns. This was demonstrated successfully by several strategies including direct-write using atmospheric-pressure microplasmas and by reduction of pre-patterned films deposited by ink-jet printing. We also attempted to understand the fundamental mechanisms behind plasma reduction and discovered what we term an electrodiffusion mechanism whereby the plasma-driven electric field within the polymer film causes diffusion of the metal ions to the film surface where they are reduced. Below, each of the plasmas used in our studies are described in detail.

Direct current (DC) atmospheric-pressure microplasma: In Chapter 2, a direct-write technique based on an atmospheric-pressure direct-current microplasma is presented. Using this process, we fabricated electrically-conductive metal patterns at the surface of polymer films deposited on
silicon wafers. The process bears similarities with electron-beam nanofabrication, but does not require any vacuum, annealing, or complex and costly equipment. A metal ion (Ag\(^{+}\)) containing polymer (polyacrylic acid) thin film cast on silicon was patterned under a DC microplasma with flowing argon and mounted on a scanning stage. Localized reaction between the microplasma and the metal-ion containing polymer result in reduction, nanoparticle nucleation, and growth and aggregation of percolated nanoparticles to form electrically-conducting microstructures at the surface of the thin film. Various process parameters such as film thickness, scan rate and film drying time are correlated to the reduction and electrical conductivity. The studies also revealed an electrodiffusion mechanism. During this process, the surface of the polymer gets enriched with percolated metallized Ag while the concentration in the bulk gets depleted. We hypothesize that this occurs due to the presence of the electric field created by the microplasma, in contact with the polymer thin film.

*Alternating current (AC) atmospheric-pressure microplasma:* Chapter 3 presents an atmospheric-pressure alternating current (AC) microplasma for the reduction of metal-cation containing polymer films. Unlike its DC counterpart, this method can process thicker films on non-conducting substrates. In addition, the process is rapid (500 µm/sec) and produces patterns of lower resistivity (0.1 – 1 mΩ-cm). By integrating an elastomer, polydimethyl siloxane (PDMS), stretchable metal features could be fabricated. We discovered that the phenomenon of electrodiffusion still holds when the films are treated under an AC microplasma. However, the microstructure of the as-reduced films is different from those obtained under the DC microplasma. Scanning electron microscopy (SEM) images reveal that the metallized top-layer is continuous with a wrinkled surface. The process is compatible with pre-straining strategies commonly adopted for fabricating
stretchable electronics.[97,98] Using this strategy, the maximum applicable strain could be extended to 35% without appreciable loss in conductivity. Further, under strain, there was uniform development of micro-cracks throughout the patterns, indicating that the strain is delocalized and guarantees good adhesion between the metalized surface layer with the polymer under layer. This is a critical requirement for stretchable electronic circuitry.[99,100]

Correlation of plasma properties with metal-ion reduction: Both the DC and AC microplasmas are operated under an applied voltage of approx. 1-2 kV with a cathode-to-anode distance of only 500 µm. Evidently, the electric field between the electrodes are relatively strong and the plasma is locally intense. Under these geometrical restrictions, it is not feasible to insert probes such as a Langmuir probe to analyze the plasma properties. In Chapter 4, two different types of relatively large area “soft” plasmas were studied which could be more carefully characterized and controlled. In both cases, the plasma density is relatively low and the electron energy is low (T_e ~ 1-10 eV) that allows us to study the reduction phenomena with time. Through relevant current-voltage and materials analyses we show that the main factors that affect reduction of Ag^+ are charge flux, operating pressure and exposure time.

In the first part of this chapter, we show an extension of the DC plasma apparatus – where we apply an external positive bias to the anode to extract charged species from the plasma and treat the Ag^+ containing polymer thin film on Si at a very low current. This approach creates a large shower of charges that can interact with the film over a diameter of ~1 cm. By constricting the total area of exposure through shadow masking, we were able to map the intensity from the reduced areas with the discharge current and exposure time. We found that at higher currents, the pattern fidelity could not be maintained, indicating a high reaction rate and high density of charged
species. When the treatment was performed at a low current but a longer time, the pattern fidelity could be maintained, but required longer duration of exposure.

The influx of charged species can be better controlled if the plasma source is operated under different operating pressures, clean and is pulsed. For this reason, we collaborated with researchers at the Naval Research Laboratories (Washington D.C.) and analyzed the reduction under a large area plasma, operated inside a vacuum chamber and driven with a pulsed power supply. The second part of this chapter will focus on the effect of a large area e-beam generated low-pressure plasma on the Ag\(^+\) containing thin films. Further, in this reactor the exact operating conditions such as background pressure, total number of pulses, duty factor, plasma exposure time and charge flux could be measured \textit{in situ} during the experiment. The results suggest that the two main factors that can affect the reduction of the cations are operating pressure and exposure time. Further, through specific control experiments we were able to rule out the involvement of any photo-reduction.

Correlating the results of the e-beam plasma and the secondary discharge DC plasma, we find that the main factor responsible for the reduction if Ag\(^+\) cations is flux of charged species. At atmospheric pressures, the flux of charged species is controlled by the current of the secondary discharge. The total amount of reduction is controlled by the exposure time. Under low pressures and similar applied voltages, the mean free path of particles is much higher. Therefore, in the e-beam plasma and under low operating pressures we observe lower reduction compared to higher pressures. The effect of exposure time, however, remains the same.

\textit{Low-pressure plasma reduction of printed metal cations:} In Chapter 5, we present a method based on pre-printing substrates by ink-jet printing a nanoparticle-free metal salt (AgNO\(_3\)) dissolved in
a solvent (ethanol and ethylene glycol) followed by plasma treatment to reduce and form electrically-conductive patterns. Post-treatment analysis by scanning electron microscopy and X-ray diffraction revealed that after plasma treatment the printed material was completely converted into crystalline silver. Further, current-voltage characteristics of these features reveal conductivity to be $<1 \text{ mΩ-cm}$. We discovered that by tuning the plasma exposure time and operating pressure, the resultant resistivity can be altered. We successfully implemented this process for the fabrication of a RC filter whose cut-off frequency could be tuned, based on the plasma exposure time and pressure.
Chapter 2

*In situ* reduction of metal ions in metal-cation containing polymer films to produce patterned, electrically conducting features using a DC plasma

2.1 Introduction

The reduction of metal cations dispersed in a polymer film by a plasma process has been reported previously by several groups including our own.[101,102,103,104] However, electrical conduction in the reduced films or features has not yet been shown which could have potential applications as flexible or stretchable interconnects in emerging electronic, optical, and energy devices. In addition, the mechanisms for reduction and formation of metal nanoparticles has not yet been elucidated.

In this chapter, I will demonstrate that a microplasma based direct-write process can be employed to produce patterned, electrically-conductive metal patterns from a metal-cation containing polymer. Choosing the right polymer is critical to achieving electrical conductivity using the microplasma patterning process. I will demonstrate it using two water-soluble polymer systems, namely polyvinyl alcohol (PVA) and polyacrylic acid (PAA). Mixing a metal salt, silver nitrate, with the polymer in aqueous solution results in a metal ion containing polymer matrix, when cast as a thin film. Efficient and well-dispersed silver nanoparticle formation is achieved only when the metal ion interacts with the polymer chains resulting in a cross-linked gel. At sufficiently high concentrations of metal salt precursor in the original solution, the particle density can reach percolation and electrical conductivity is attained. SEM characterization of the films reveals that the nanoparticle formation is limited to the surface of the films. We propose an electrodiffusion model based on the electric migration of metal cations to the negatively-based
plasma to explain this surface enrichment. Overall, by tailoring the film composition, plasma parameters, and finally the film thickness, it is possible to produce relatively high electric conductivities of $1 \text{ m}\Omega\text{-cm}$ which is comparable to printed metal structures,[105,106] polymer nanocomposites,[107,108] and indium tin oxide (ITO).[109]

2.2 Experimental procedure

2.2.1. Preparation of silver ion imbibed polyvinyl alcohol (Ag-PVA) thin films

Process schematic of Ag-PVA thin film preparation is shown in Figure 2.1. 1% w/w polyvinyl alcohol (PVA, M.W. = 100 K, Acros Organics) was dissolved in water to prepare the base solution. Requisite molar concentration of silver nitrate ($\text{AgNO}_3$, Acros Organics) was dissolved in this mixture to prepare the silver ion containing solution. The solution was drop cast as a thin film on n-type $<100>$ Si and dried overnight in open air to prepare thin films.

![Figure 2.1](image.png)

**Figure 2.1.** Graphic representation of process flow for preparation of Ag-PVA thin films by drop casting method.
2.2.2. Preparation of silver ion imbibed polyacrylic acid (Ag-PAA) thin films

A process flow schematic for the preparation of thin films of polyacrylic acid (PAA) loaded with silver cations (Ag⁺) from aqueous solution is depicted in Figure 2.2. PAA (Acros Organic, M_w = 1,260,000) was dissolved in 100 ml of 1:3 v/v deionized water:ethanol at 0.255% w/v. Silver nitrate (AgNO₃, >99.9% purity, Alfa Aesar) dissolved in 10 ml of the same solvent was added to the solution and stirred vigorously for 10 minutes. An additional 150 ml of ethanol was then added to this mixture and left to stir for another 15 min to produce a milky white solution. Centrifuging at 21,000 G for 30 mins resulted in the formation of a white precipitate containing the PAA and Ag⁺. The precipitate was separated by decanting the clear supernatant and homogenized in 13:4 v/v water:ethylene glycol at 10-20% w/w (Cole Parmer, LabGen 7). The resulting fluid was kept in vacuum (~20 psi) for a minute to remove air bubbles and then cast with a doctor’s blade on n-type silicon (Si) (100) wafers, dried overnight, and finally vacuum dried for 2 hr before microplasma exposure. The Ag concentration in the deposited film was calculated as the molar ratio of Ag⁺ to repeat units of PAA, i.e., \( \{(\text{CH(COOH)CH}_2)\} \), represented as [COOH]⁻, in the solution. For example, a film containing \( \text{Ag}^+:[\text{COOH}]^- = 1:1 \) indicates that 169.87 g of AgNO₃ was mixed with 72 g of PAA in solution.
Figure 2.2. Schematic process flow diagram for preparation of Ag-PAA thin films on silicon. 
AgNO₃ is mixed in an aqueous solution of PAA resulting in chelation of Ag⁺ with COOH⁻. The precipitate (Inset optical image) is homogenized and cast as a thin film with a doctor’s blade. Ag⁺ concentration in the PAA thin films is specified as the molar ratio of Ag⁺ and COOH⁻ assuming that the PAA is completely hydrolyzed.

2.2.3. DC microplasma patterning

To fabricate metallic patterns, the Ag-PAA film was exposed to a scanning, non-thermal, atmospheric-pressure direct-current (DC) microplasma. Details of the experimental setup are shown in Figure 2.3. The microplasma was formed in a flow of argon (Ar) gas expanding into open air between a 1/16” inner diameter stainless steel capillary tube (Restek Inc.) electrically biased at a negative high voltage and a substrate at a floating ground potential on the anode side. The electrode gap was fixed in all experiments to be 500 µm and typical voltages and currents at the power supply were ~700 V and 1 mA, respectively. Current in the microplasma was measured from the voltage drop across a 500 Ω resistor connected in series between the substrate and physical ground. The microplasma was scanned across the film by moving the substrate with two
computer-controlled stepper motors. For a scan rate of 0.25 mm/sec, an average line width of 300 µm was obtained and most of our characterization was performed on single lines 5 mm in length.

![Diagram of DC microplasma apparatus with programmable stage for polymer patterning]

**Figure 2.3.** Schematic representation of DC microplasma apparatus with programmable stage for polymer patterning

### 2.2.3. Characterization of microplasma drawn lines

Scanning electron microscopy was performed on the plasma-treated samples after sputter coating them with a 5 nm thick Pd layer to improve conductivity (while the lines may be conductive the other areas of the film were not). SEM, focused ion beam (FIB) etching, and energy dispersive spectroscopy (EDX) were performed with a FEI Nova Nanolab 200 field emission gun SEM. Both plan and cross-sectional analysis of the films was carried out. Details for the sample preparation are schematically shown in Figure 2.4. After microplasma patterning, the films were
either imaged directly on the substrate from the top or cleaved with a razor blade and mounted vertically, exposing the cross-section to the SEM gun. EDX line scans and maps were also obtained across this cross-section.

**Figure 2.4.** Process schematic for SEM and EDX characterization of sample cross-section after microplasma patterning

Electrical characterization was performed using a 2-point probe method inside a Faraday chamber with a 2-point probe setup using a Keithley 4200 SCS source which can precisely measure resistances ranging from $10^{-6}$ – $10^{12} \, \Omega$. The electrical circuit for the 2-point probe measurement coupled with an optical image of the probe is shown in Figure 2.5. After microplasma exposure, the processed film was peeled off from the Si substrate and placed on an insulating substrate such as glass or polyethylene terephthalate (PET). Conductive Ag paste was used to deposit contact pads on the microplasma-reduced features for current-voltage (I-V) measurements. The value of resistance was obtained from the slope of the I-V plots and the cross-sectional area of the pattern was obtained from SEM to calculate bulk resistivity of the features. For each value of resistivity over 20 samples were analyzed to specify an appropriate standard deviation and an average resistance.
**Figure 2.5.** Electrical circuit for I-V measurement of microplasma drawn features. The probe-tips are connected to the patterned features through conductive silver paste.

### 2.3. Results and discussions

A key part of this study was the selection of a metal and polymer to be exposed to the scanning microplasma process to obtain electrically-conductive patterns. We focused on water-soluble metal salts and polymers that are widely used, safe, low cost, and easy to solution process. We chose Ag as the metal, which is an excellent conductor, easy to reduce [standard reduction potential = 0.799 V vs. standard hydrogen electrode (SHE)], and significantly less expensive than Au, and AgNO$_3$ as the metal source, which is low cost and water soluble. We initially tried polyvinyl alcohol (PVA) as the polymer which is also water soluble and therefore could be mixed with AgNO$_3$, and critically, was not found to reduce AgNO$_3$ in solution like other water soluble
polymers such as polyvinyl pyrolidone (PVP) [110,111]; if the AgNO₃ is reduced in solution, the plasma plays no role and, more importantly, patterns of metallized lines could not be prepared by plasma exposure.

Results for films cast from aqueous solutions of PVA and AgNO₃ and exposed to the microplasma are shown in Figure 2.6. A representative SEM image in Figure 2.6(a) reveals that a line with a width of approximately 300 μm is created, and the corresponding EDX false color maps of Ag and C of the same area in Figures 2.6(b) and (c), respectively. The EDX maps are false colored with the intensity corresponding to the Ag and C content in the film. These images confirm that microplasma exposure produces Ag rich layer. At higher magnification, Figure 2.6(d) shows that the film is made up of aggregated particles that are only semi-continuous. Figure 2.6(e) shows the I-V characteristics of the line measured by a two-point probe measurement. A lower resistance is obtained after microplasma exposure. However, the resistance measurement shows that the resistance of these 1 cm long lines decrease from 10 MΩ to only 120 kΩ, which is appreciably large for any electrical good-conductor.
Figure 2.6. (a) Low resolution SEM image of a microplasma patterned feature on the surface of a drop casted Ag-PVA thin films on a Si substrate. The scale bar is 500 µm; (b) EDX false color image of Ag distribution at the surface of Ag-PVA film shown in (a); (c) EDX false color image of carbon after microplasma patterned area shown in (a); (d) High resolution SEM image of a microplasma patterned area showing particles formation; (e) Comparison of I-V characteristics of a 5 x 0.3 mm line patterned with the microplasma (green) with that of an un-patterned area (black); (f) Optical image of a vial containing 500 mM Ag in 1% PVA in water showing characteristic brown solution due to decomposition of Ag$^+$ to Ag$^0$ nanoparticles naturally over 1-2 days.
The relatively high resistance can be explained by the microstructural analysis shown in Figure 2.6(d). Many of the nanoparticle aggregates are isolated and do not percolate to produce conductive paths, leading to a high resistance. It may be possible to overcome this issue by increasing the AgNO\textsubscript{3} concentration in the solution mixture and, thus, increasing the particle density in the film after plasma reduction. However, high concentrations of AgNO\textsubscript{3} were found to get spontaneously reduced to Ag nanoparticles when combined with PVA in solution [Figure 2.6(f)] because PVA is a weak reducing agent [112,113]. This limits the applicability of PVA as a supporting polymer for the fabrication of Ag patterns by our strategy.

It has been previously reported that polyelectrolytes such as polyacrylic acid (PAA) can electrostatically bind with different metal cations, including Ag\textsuperscript{+}, through its carboxylic acid (-COOH) side chains.[114,115,116] We hypothesized that this specific molecular interaction could enable the preparation of well-dispersed and semi-organized films of Ag\textsuperscript{+} that when reduced would lead to improved percolating networks of Ag nanoparticles. However, the same electrostatic interaction of Ag\textsuperscript{+} with COOH\textsuperscript{-} groups leads to chelation and reduces the solubility in polar solvents such as water and ethanol which required additional steps involving separation of the solid phase, homogenizing, and deposition by doctor’s blade. Figure 2.7(a) shows an image of the Ag\textsuperscript{+}-PAA gel/precipitate after separation from the supernatant. Casting using a doctor’s blade produces a semi-transparent film containing only the polymer and Ag\textsuperscript{+}. Exposing to the microplasma results in a clear color change attributed to the formation of metallic Ag at the surface of the film [Figure 2.7(b)]. X-ray diffraction (XRD) confirmed that the patterned line consisted of crystalline Ag [Figure 2.7(c)].
Figure 2.7. (a) Optical image of Ag-PAA after formation of gel and separation (Ag$^+:[\text{COOH}]^-$ = 0.64). (b) Optical images of microplasma patterned Ag-PAA films. (c) XRD of Ag-PAA films (Ag$^+:[\text{COOH}]^-$ = 0.64) showing the formation of crystalline Ag after microplasma exposure.
In order to ensure high conductance and percolating nanoparticles in the microplasma patterned features, experiments were performed with increasing silver concentration in the polymer matrix. A representative high magnification scanning electron microscope (SEM) image of a patterned line on a film containing Ag$^+:[\text{COOH}]^-$ = 0.3 and 0.64 respectively [Figures 2.8(a) and 2.8(b)] reveal the presence of particles within the feature. They show that at a relatively low concentration, Ag nucleates homogeneously throughout the pattern. At a higher Ag precursor concentration in the PAA matrix, these particles form a continuous network. We similarly prepared 8 μm thick Ag-PAA films containing different ratios of Ag$^+:[\text{COOH}]^-$ ranging from 0.32:1 to 0.64:1. The continuity of the percolation in the films with higher Ag concentration is evident from the electrical properties of the pattern. Figure 2.8(c) shows I-V characteristics of the 5 mm long patterned lines produced upon exposure to the microplasma, measured by two-point probe measurements. With increasing concentration of Ag$^+$ in the polymer, the resistances determined from the average slope were found to decrease from 32 MΩ to 3 kΩ, consistent with higher Ag$^+:[\text{COOH}]^-$ ratios leading to more conductive metal networks being formed.

**Figure 2.8.** SEM images of microstructure of Ag-PAA film with Ag$^+:[\text{COOH}]^-$ concentrations of (a) 0.32 and (b) 0.64, and (c) Current-voltage characteristics of microplasma-reduced 5 x 0.3 mm lines on 8 μm thick films containing different Ag$^+:[\text{COOH}]^-$ ratios.
To further examine the microplasma-treated lines and understand the nature of the particle formation and conductivity, we carried out additional SEM and energy-dispersive spectroscopic (EDX) analyses. Figures 2.9(a) and 2.9(b) show SEM images and corresponding EDX maps of lines fabricated by microplasma exposure from a relatively low Ag concentration (Ag⁺:[COOH]⁻ = 0.32) film. The high intensity of Ag confirms the enrichment of Ag by microplasma exposure [Figure 2.9(b)]. In order to analyze the concentration of Ag within the film, a 5 µm deep trench was produced across the patterned line by a focused ion beam (FIB). The EDX map suggests that the Ag concentration decreases below the surface [Figure 2.9(b)]. In order to carefully characterize the concentration depth profile, films were cut and cross-sectional SEM images and corresponding EDX false color intensity maps were obtained [Figure 2.9(c)-2.7(h)]. The cross-sectional images show high surface concentration of Ag, confirming that the formation of Ag particles is localized near the surface [Figure 2.9(c) and 2.9(d)]. This is further supported by images near the edge of a patterned line that show the non-uniform Ag concentration only occurs in the exposed part of the film [Figure 2.9(e) and 2.9(f)]. Images of the unexposed region of the same film show that before plasma exposure, the initial Ag concentration is homogeneous throughout the film depth [Figure 2.9(g) and 2.9(h)].
Figure 2.9 (a) SEM image of a microplasma-reduced line in Ag-PAA. The center of the line was etched by FIB. (b) EDX false color map of Ag in the region shown in (a). (c) Cross-sectional SEM
image of microplasma-reduced region. (d) EDX false color map of Ag in (c) showing higher concentration of Ag at the surface. (e) Cross-sectional SEM image at the boundary of a microplasma-reduced line. (f) EDX false color map of Ag in (e) showing higher surface concentration of Ag only in the microplasma exposed region. (g) Cross-sectional SEM image of an unexposed region of the same sample analyzed in (c) – (f). (h) EDX false color map of Ag in (g) showing uniform distribution of Ag.

The cross-sectional images were semi-quantitatively analyzed by plotting the intensity of the EDX line scan as a function of film depth (Figure 2.10). SEM images of the EDX scan areas are also shown in Figure 2.10 for reference. The analysis shows that in the native film, the Ag and C concentrations are constant throughout the film at an atomic percent of 25 at% Ag and 50 at% C. The Ag concentration rapidly increases after microplasma exposure at the film surface to ~75 at%, and, simultaneously, the C concentration decreases to ~25 at%. The Ag concentration remains constant at 75 at% upto ~5 μm from the surface and then rapidly decreases to its original value in the lower part of the film, i.e., ~25 at%, at a depth of ~10 μm. Near the base of the film, the C concentration increases to ~75 at% and the Ag concentration is depleted to ~10 at%.
Figure 2.10. Cross-sectional SEM images of Ag-PAA films before (top) and after (bottom) microplasma reduction and corresponding normalized atomic weight of Ag and C through the film depth, as obtained by EDX line scans. Scale bar is 20 μm.
Previous studies have shown that metal nanoparticles can be formed from metal salts dispersed in a polymer film by plasma exposure.\[117\] The mechanism that has been suggested is reduction of metal cations by electrons. Since electrons created in a plasma are low energy and have a relatively small skin depth, the enrichment of Ag at the surface and simultaneous depletion of Ag at the base of the film after microplasma exposure suggest that surface reduction alone cannot explain the formation of an Ag-rich surface layer. We propose that Ag ions within the bulk of the film diffuse to the surface during microplasma exposure to supply metal precursor for continued growth. The DC microplasma process produces an electric field within the film oriented with a negative pole at the surface and a positive pole at the base. This electric field may drive diffusion of the positively charged Ag\(^+\) ions to the film surface as in the case of ion migration in polymer systems.\[118,119\] The coordination of Ag\(^+\) to PAA is reversible\[115\] and the electric field should present a strong enough force to pull the Ag\(^+\) ions to the film surface where they can undergo reduction by electrons from the microplasma. It is possible that the polymer may undergo some morphological changes during this process; however, it still acts as a supporting backbone to the Ag layer on the surface. Further, other factors such as the plasticizer content and microplasma scan rate can also affect the amount of silver precipitating at the surface after microplasma patterning. To validate this qualitative picture, we processed films of a low Ag content (Ag\(^+\):[COOH]\(^-\)=0.32) with systematic variation of process parameters. These experiments are detailed below, categorized by the parameter that was changed.

\textit{a. Varying film thickness:} The measured EDX intensity is proportional to the Ag density in the film, suggesting that Ag\(^+\) is reduced and precipitated only at the surface of the film during microplasma exposure. To understand how the Ag is reduced and precipitated at the film surface,
we carried out microplasma treatment on films of varying thickness. All films were identically prepared with an Ag$^+$ to PAA ratio of 0.3, drying for 24 h, and scanning at a rate of 500 μm/s. Figures 2.11(a) – 2.11(d) show EDX line scans of the Ag content in films of initial thicknesses of 15, 25, 70, and 110 μm, respectively. In all cases, microplasma exposure led to the enrichment of Ag in a near surface region. The thickness of this region within the film increased slightly from 2 to 15 μm with increasing film thickness. The increase in surface Ag concentration was accompanied by a depletion of Ag at the base of the film.

Figure 2.11. EDX line scan of Ag-PAA films with thicknesses of (a) 15 μm (b) 25 μm (c) 65 μm and (d) 110 μm
Figure 2.12 shows I-V curves of the same films characterized by cross-sectional SEM and EDX in Figure 2.11 obtained by two-point probe measurements on 5 mm long lines. As the thickness of the film was increased, the conductivity of the scanned lines was observed to increase, as indicated by the decrease in the slope of the I-V measurements. The corresponding absolute resistances shown in Table 2.1 are found to decrease from ~14 MΩ to ~80 kΩ as the film thickness increased from 10 to 80 µm. In addition, the error in the measurements decreases with film thicknesses, reflecting the increase in reproducibility.

Figure 2.12. Two point probe current-voltage (I-V) measurements of 0.3 x 5 mm long microplasma reduced lines fabricated in Ag-PAA films of varying thicknesses. The films were dried for 24 h and the microplasma was scanned at a rate of 500 µm/s
Table 2.1: Summary of resistances obtained by two-point probe current-voltage measurements of 0.5 x 5 mm long lines fabricated by microplasma reduction of Ag-PAA films as a function of initial film thickness, microplasma scan rate, and drying time for the film.

<table>
<thead>
<tr>
<th>Film thickness (μm)</th>
<th>Scan rate (μm/sec)</th>
<th>Drying time (h)</th>
<th>Resistance (MΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>500</td>
<td>24</td>
<td>14.2 ± 7.3</td>
</tr>
<tr>
<td>20</td>
<td>500</td>
<td>24</td>
<td>2.2 ± 1.5</td>
</tr>
<tr>
<td>40</td>
<td>500</td>
<td>24</td>
<td>0.67 ± 1.6</td>
</tr>
<tr>
<td>80</td>
<td>500</td>
<td>24</td>
<td>0.12 ± 0.17</td>
</tr>
<tr>
<td>80</td>
<td>500</td>
<td>48</td>
<td>0.52 ± 1.3</td>
</tr>
<tr>
<td>80</td>
<td>500</td>
<td>72</td>
<td>0.95 ± 38.0</td>
</tr>
<tr>
<td>40</td>
<td>250</td>
<td>24</td>
<td>0.56 ± 0.99</td>
</tr>
<tr>
<td>80</td>
<td>250</td>
<td>24</td>
<td>0.81 ± 0.55</td>
</tr>
<tr>
<td>40</td>
<td>125</td>
<td>24</td>
<td>0.83 ± 0.10</td>
</tr>
<tr>
<td>80</td>
<td>125</td>
<td>24</td>
<td>0.33 ± 6.4</td>
</tr>
</tbody>
</table>

Based on the SEM and EDX characterization and I-V measurements, we present a picture of the reduction of Ag-PAA films by the microplasma process. Initially, the films contain Ag⁺ at a uniform concentration through the film bulk, but the total mass amount is higher with increasing film thickness. When the films are exposed to the microplasma, the Ag⁺ is reduced at the surface. We have previously shown indirect evidence that electrons in the plasma play an important role in reducing Ag⁺ [120,121]. Additionally, Ag⁺ from the film bulk can also be driven to the surface to be reduced because of an electric field created by the microplasma. The microplasma is negatively-biased with respect to the ground electrode at the base of the film which should produce an electric
field with a negative pole at the top of the film and a positive pole at the bottom. We acknowledge that the field strength is not known because of the voltage drops across the microplasma. Based on the nature of the microplasma, which is a direct-current plasma, and at the voltages and currents that are used, we can assume operation in a glow discharge mode [122]. Thus, the voltage at the film surface is most probably proportional to the anode sheath potential. The difference between this sheath potential and ground is the actual potential drop across the film that guides the ions from the bulk to the surface. There is also a question regarding the nature of transport of the Ag\textsuperscript{+} in the polymer film which we will address in one of the following sections on varying drying time. Nonetheless, our proposed mechanism supports both why exposing the films leads to a surface-rich layer of Ag and why the thickness of this layer and, thus, the resistance of the features, depend on the film thickness. The film essentially acts as a reservoir of Ag\textsuperscript{+} for the surface-mediated reduction process. Additionally, a factor that can influence this diffusion process is the time scale of the interaction between the microplasma and the film, which is determined by the scan rate. This is addressed in the following section.

\textit{b. Varying microplasma scan rate:} The microplasma scan rate was varied on 80 μm thick films that were dried for 24 h and contained a fixed ratio of Ag\textsuperscript{+} to PAA of 0.3. Figure 2.13(a) shows cross-sectional EDX line scans on the films with increasing scan rates from 125 to 500 μm/s. In all cases, there is an enrichment of Ag at the surface. As the scan rate was decreased, the peak intensity of Ag and the thickness of the surface-rich layer increase. This is explained by the increase in the interaction time between the microplasma and a given position in the film which results in increased reduction and increased migration of Ag\textsuperscript{+} to the surface, the latter based on our proposed mechanism. In addition, optical image [Figure 2.13(b)] shows that at slower scan rates, the width of the patterned features increased. On further reduction of scan rate to <100 μm/sec
lateral interaction of the field with the microplasma increased to an extent that the pattern fidelity could not be maintained [Figure 2.13(c)].

**Figure 2.13.** (a) EDX line scans of 80 μm thick films at varying microplasma scan rates. All films were dried for 24 h. (b) Optical images of patterned features drawn at 125 μm/sec (left) and 250 μm/sec (right), (c) Optical image of pattern drawn at 60 μm/sec. Two-point probe current-voltage (I-V) measurements on 0.5 x 5 mm long microplasma reduced lines fabricated at varying scan rates in Ag-PAA films of thicknesses (d) 40 μm & (e) 80 μm. All films were dried for 24 h.

Electrical measurements of lines produced at different microplasma scan rates are shown in Figures 2.13(d) and 2.13(e). Two different film thicknesses of 40 and 80 μm were analyzed.
From the I-V traces, the resistances are found to decrease with increasing film thickness at all scan rates, consistent with the previous part of our study. The minimum bulk resistivity is estimated to be \( \sim 4 \pm 0.2 \, \Omega \cdot \text{cm} \) for 80 \( \mu \text{m} \) thick films, dried for 24 hrs and scanned at 250 \( \mu \text{m/sec} \), based on a reduction depth of 5 \( \mu \text{m} \) from EDX analysis (see Figure 2.11). The dependence of the resistance on scan rate is more complicated. At very high and very low scan rates, the resistance is large, and is lowest at the intermediate scan rate. As previously shown by cross-sectional EDX analysis, at very high scan rates, the interaction time of the microplasma and the film at any given position is extremely short and very little Ag\(^{+}\) is reduced or drawn to the surface. At the very low scan rates, cross-sectional EDX analysis indicates that there is more reduction because of the increased time the microplasma spends in contact with the film, but the line width is not maintained. Further, Table 2.1 shows that for very high and low scan rates, the errors in the measured resistances are large. We suggest that at low scan rates, more Ag\(^{+}\) is reduced, but this leads to particles growing larger rather than increased nucleation of particles to increase the particle density. If fewer large particles are formed, the particles may be locally isolated and sufficient percolation may not be obtained to produce conductivity.[123]

c. **Varying drying time – Effect of plasticizer:** Our proposed mechanism for the migration of Ag\(^{+}\) in the polymer matrix suggests that the diffusive properties of the film are important. We note that this diffusion refers to the transport of ions in an electric field, which we term electrodiffusion. In general, the diffusivity of mobile species in a polymer film is related to its physical properties such as the rigidity (or conversely flexibility) and cross-linking of the polymer chains. As previously described, PAA is known to cross-link with the addition of metal cations including Ag\(^{+}\). To overcome this cross-linking which occurred during our solution preparation, a solvent was added (water/ethylene glycol) which acts as a plasticizer and swells the polymer film. The expansion of
the polymer film should have the effect of increasing its permeability and, therefore, enhance the
diffusion of metal ions.[124] During our preparation of films, we have observed that a key step is
the drying of the film which reduces the plasticizer in the film and may reduce diffusion. This was
quantified by thermogravimetric analysis (TGA) of the initial films (before microplasma
exposure). Figure 2.14(a) shows the TGA spectrum of a pure, completely dried PAA film for
reference. The differential TGA curve shows peaks at temperatures of 220 and 300 °C, which
correspond to the known decomposition of carboxylic acid side chains and the hydrocarbon
backbone in PAA, respectively.[125] Complete carbonization of the polymer residue and
decomposition of AgNO₃ occurs between 400-500 °C.[126] Figures 2.12(b)-(d) are the TGA
spectra of 80 μm thick films containing 0.3 Ag:PAA dried for periods of 24, 48, and 72 h,
respectively, in ambient room air. All the films exhibit initial mass loss at 100 °C from residual
water in the film. A sharp peak at 180 °C is observed in the film dried for 24 h, corresponding to
the presence of ethylene glycol [Figure 2.14(b)]. After 48 h, the intensity of this peak decreases
because of some evaporation [Figure 2.14(c)]. The ethylene glycol is completely evaporated in
films dried for 72 h, as indicated by the absence of any peak at 180 °C, and a new peak is observed
at 200 °C [Figure 2.14(d)], which has been previously reported for completely cross-linked Ag-
PAA films and is related to Ag⁺:COO⁻.[125] These results confirm that with increasing drying
time, the residual amount of ethylene glycol in the film decreases, the cross-linked polymer chains
collapse, and the polymer matrix (film) becomes more rigid.
Figure 2.14. Thermogravimetric analysis (TGA) spectra (black) and differential spectra (Blue) of (a) pure PAA and unreduced Ag-PAA films containing a Ag⁺ to PAA ratio of 0.3 and dried at 69% relative humidity and ambient temperature of 60 – 70 °F for (b) 24 h, (c) 48 h and (d) 72 h.

To correlate the effect of residual solvent and therefore, the permeability of the Ag-PAA films on the microplasma reduction process, films with a constant thickness of 80 μm and Ag⁺ to PAA ratio of 0.3 were dried for varying times and then exposed to the microplasma at a fixed scanning rate of 500 μm/s. Cross-sectional EDX line scans in Figure 2.15(a) show that while the peak Ag intensity is relatively independent of the drying time, the thickness of the surface-rich layer increases with decreasing drying time. Interestingly, for completely dry films (72 h), there is
a region of ~30 µm near the surface of the film where the Ag content in the film is significantly depleted. These results show the role of the residual solvent on the diffusion of Ag\textsuperscript{+} through the film. For a drying time of 24 h, significant residual ethylene glycol is present in the films, as shown by TGA measurements, which can act as a plasticizer and enhance the permeability in the films to allow Ag\textsuperscript{+} to diffuse from the bulk to the surface, resulting in depletion of Ag\textsuperscript{+} throughout the film. After 48 h, the depletion of Ag\textsuperscript{+} through the film is slightly reduced. Drying for 72 h leads to complete removal of the ethylene glycol, again shown by TGA measurements, and the films become rigid and less permeable to Ag\textsuperscript{+} diffusion. The Ag\textsuperscript{+} that is initially near the surface is still able to be reduced, but there is less depletion through the bulk of the film. Additional support for this argument is provided by I-V measurements [Figure 2.15(b)] which show that increasing drying time from 24 to 72 h results in a significant decrease in the slope of the plot. The corresponding resistances of the features vary from about 0.5 to 1 kΩ respectively (Table 2.1). However, for completely dried films (72 hrs), there is a significant increase in the associated measurement error. With minor variations in ambient conditions like temperature and humidity, the trace amount of residual plasticizer can vary and, thus, the amount of Ag\textsuperscript{0} precipitating at the surface changes non-systematically.
**Figure 2.15.** (a) EDX line-scan of microplasma reduced lines fabricated at a scan rate of 250 μm/s on 80 μm thick Ag-PAA films dried for different lengths of time. (b) Two-point probe current-voltage (I-V) measurements on 0.5 x 5 mm long microplasma reduced lines fabricated in 80 μm Ag-PAA films dried for different lengths of time

**d. Electric field effects:** To further study the electrodiffusion of Ag⁺ in our films to produce electrically-conductive features, we attempted to vary or control the electric field in the film. However, as previously noted, the electric field is strongly coupled with the operation and properties of the microplasma, making it difficult to have independent control. We instead designed a control experiment shown in Figure 2.16(a) where we fabricated a counter electrode such that in addition to the electric field perpendicular to the film, one in plane with the film is created. By making the films relatively thin, we assume that the in-plane diffusion of Ag⁺ is slower and, thus, can be observed. We note that in comparison to the typical electrode geometry at the base of the films, the Ag-PAA films are identical and assuming that diffusion of Ag⁺ is isotropic,
there should be no difference in the transport of Ag\(^+\) in plane vs. perpendicular to the film. However, the electric field strength was lower for the in-plane experiments because of the distance between the Pd electrodes which was 1 cm and much larger than the distance of the base electrode which was equal to the thicknesses of the films that were studied, \(\sim 10-100 \, \mu\text{m}\).

**Figure 2.16.** (a) Process flow diagram for fabrication of electrodes in a planar geometry, (b) Representative optical image of Ag formation in a lateral direction as a result of fixed microplasma
exposure for 1 min at the center of a Ag-PAA film that was dried for 24 h on a planar electrode, (c) Mean lateral spread of Ag as a function of reduction time from the center of Ag-PAA films with a planar electrode dried for different lengths of time

Experiments with the in-plane electrode geometry were carried out by exposing the films to the microplasma at a fixed position for different times. Figure 2.16(b) shows a representative optical image of a film dried for 24 h and exposed to the microplasma at its center for 30 s. The in-plane transport of Ag is clearly observed. We repeated these experiments on films dried for varying times and plotted the area of Ag reduction as a function of microplasma exposure time in Figure 2.16(c). The reduced area was estimated by capturing images with an optical microscope and analyzing the images with ImageJ. Our results show that with increasing drying time, the rate of growth in the lateral direction decreases, in agreement with the reduced transport of Ag$^+$ as the plasticizer is removed that was also observed for experiments with the electrode at the base of the film.

Diffusion is a well-known phenomenon in electrochemical systems, typified by movement of particles due to density gradients. However, it is mostly associated with liquid and gaseous phases.[127] In solid electrolytes, movement of particles is usually referred to as migration.[128] On the other hand, in the presence of electric field, electromigration is term that refers to migration of grain boundaries.[129] Additionally, electric migration is usually associated with electrophoretic migration of charged macromolecules such as proteins.[130] Since none of these cases can justify the temporal non-linearity in the rate of movement of ions in our thin film [Figure 2.16(c)], we use the term electrodiffusion to explain the plasma induced enrichment of Ag at the surface of the thin film.
The figure of merit for electrical conductivity is bulk resistivity. Bulk resistivity can be calculated from the geometry of the microplasma drawn line. However, the thickness of our reduced lines is not the original film thickness, but some surface layer that is on the order of ~5-10 µm thick, based on cross-sectional EDX analysis (see Figure 2.11). Figure 2.17(a) shows the resistance of 5 mm long features that were 300 µm wide, as a function of the original film thickness after microplasma exposure for two different ratios of Ag⁺:[COOH]⁻. For thin films (<10 µm), the Ag loading in the film volume or the exposure time (scanning rate) is too low for the Ag to diffuse to the surface and react to form a percolated network. Beyond a critical thickness of approximately ~12 µm, the bulk resistivity of the microplasma-reduced lines decreases dramatically and becomes independent of the film thickness (~ 1-5 mΩ-cm), indicating that the Ag mass in the bulk is high enough to electrodiffuse, react and percolate within the time scale of microplasma exposure to form a percolated network. These results indicate that the bulk resistivity reaches a maximum at a sufficiently large film thickness, independent of the initial Ag⁺:[COOH]⁻ concentration. Thus, the bulk resistivity can be optimized for any given Ag⁺:[COOH]⁻ concentration. Figure 2.17(b) shows the maximum bulk resistivity obtained on films with Ag⁺:[COOH]⁻ ratios of 0.32:1, 0.48:1, 0.57:1 and 0.64:1, respectively, and thicknesses >20 µm. The calculated bulk resistivity value is between 1 to 5 mΩ-cm irrespective of the precursor Ag⁺ concentration. As a reference, the bulk resistivity of pure Ag is 1.6 µΩ-cm.
Figure 2.17. (a) Average resistance of 5 x 0.3 mm features as a function of original film thickness at two concentrations of Ag$^+$:[COOH]$^-$. (b) Maximum average bulk resistivity for films of different Ag$^+$:[COOH]$^-$ concentrations. All films had original thicknesses >20 μm.

2.4. Summary

In summary, we have developed an ambient direct-write process to produce electrically conductive lines at the surface of polymer films. Materials analysis and control experiments indicate that percolating networks of particles are formed by electrodiffusion of Ag ions from the bulk film to the surface and microplasma reduction. The reduction phenomenon and resulting electrical conductivity of metal cation-containing polymer films is shown to depend on film thickness, microplasma scan rate, drying time, and direction of electric field. Increasing the thickness of the film increases the total amount of Ag$^+$ available to diffuse to the surface and be reduced to form conductive metal. The scan rate controls the interaction time of the microplasma and the film with lower scan rates leading to increased reduction and diffusion. The drying time affects the presence of a plasticizer in the film which is shown to enhance electrodiffusion. By
optimizing these parameters, the surface conductivity is maximized independent of metal loading, which may be desirable to reduce overall metal content while producing conductivity where it is desirable for many flexible conductor applications, at the surface of the film.
Chapter 3

Fabrication of stretchable, electrically-conductive features by AC-based plasma reduction

3.1. Introduction

The ability of a microplasma-based direct-write process to produce electrically-conductive features at the surface of polymer films by *in situ* reduction of metal-cation containing polymers is particularly attractive for the fabrication of stretchable electrical conductors. A general issue with stretchable electrical conductors is that when electrically conductive metals are combined with flexible or stretchable polymers, stress at the interface of the two materials leads to localized strain that ultimately breaks electrical continuity. By reducing and forming the metal from within the polymer matrix, it may be possible to improve the adhesion between the metal and the polymer and thus mitigate strain and maintain electrical conductivity under applied deformation. However, two limitations of the materials process we presented in Chapter 2 are 1) the polymer that was studied, PAA, is not necessarily stretchable and 2) the DC operation of the plasma does not allow the processing of thick films which would be needed to obtain robust and free-standing films that could be stretched and implemented in applications. [131]

In this chapter, we addressed these issues by extending our plasma process to alternating current (AC) power which allowed the processing of thick insulating polymer films (>100 μm). We integrated the Ag-PAA films with an elastomeric polymer, polydimethylsiloxane (PDMS), to create a stretchable platform for the formation of electrically-conductive features. We thus successfully show that electrically conductive features can be produced by AC plasma treatment of Ag-PAA films on top of a PDMS substrate; in fact, the films are even more conductive than DC
plasma treatment with a bulk resistivity of 1.5 mΩ-cm. Stretching studies reveal that the films exhibit negligible change in resistance up to 10% uniaxial strain. To further improve this result, we incorporated prestraining which is a commonly used strategy to improve the overall strainability of electrically-conductive features on elastomers.[132,133] After prestraining films to 35%, we could maintain conductivity with negligible change in resistance up to applied strains of 35%. The electrical properties of all the films were also found to be fully reversible when strain was removed. To explain the electrical performance of the films, we carried out scanning electron microscopy (SEM) analysis which showed that strain is highly delocalized, producing microcracks distributed evenly throughout the film surface as the films are stretched. We suggest that this is achieved by excellent interfacial adhesion which is uniquely created by the nature of the growth of the percolated metal layer from within the polymer itself.

3.2 Experimental methods

3.2.1. Preparation of PDMS films

PDMS films were made from Sylgard 184 (Dow Corning) two-part epoxy with 1.5 g base and 0.1 g cross-linker. The mixture was drop cast on 100 mm <100> Si wafers with 300 nm SiO₂. The film was degassed and heated for 10 min at 150°C, followed by a low-pressure O₂ plasma cleaning (Nordson March) for 45 sec. The latter step renders the surface hydrophilic which was found to improve adhesion of the Ag-PAA layer.
3.2.2. Preparation of Ag-PAA films

AgNO₃ and PAA (Mᵥ = 1.25 MM, Sigma-Aldrich) were dissolved in a solution of 1:3 v/v water:ethanol and stirred rapidly for 2 min. The milky white solution was centrifuged at 21,000 G (Beckman coulter, Allegra 25R) for 30 min to produce a precipitate. After removing the supernatant, the precipitate was homogenized (LabGEN 7, Cole Parmer) with a 1 ml solution containing ethylene glycol and water at 4:13 v/v. The homogenized paste was degassed and cast on top of the hydrophilized PDMS film by doctor’s blade casting technique (MTI Inc.). The films were then dried overnight. A schematic of steps followed for the fabrication of Ag-PAA/PDMS film stacks is shown in Figure 3.1.

Figure 3.1. Flow diagram of preparation of PDMS for coating with Ag-PAA. AgNO₃ is dissolved in a solution of PAA and centrifuged to retrieve the precipitate. The recovered precipitate is homogenized and then cast on hydrophilized PDMS.

3.2.3. Microplasma treatment

The Ag-PAA/PDMS film stacks were treated by an AC-powered atmospheric-pressure microplasma formed in a flow of helium (He) gas between a stainless steel capillary and an aluminum electrode at the base of the film to produce electrically-conductive features. The capillary tip was separated from the film surface by a gap of 500 μm. PDMS is a high dielectric
material and provides high resistance to the flow of DC current. A schematic representation comparing the DC and the AC circuits is shown in Figure 3.2. Detailed explanation of the DC circuit is given in section 2.2.3. For the AC circuit, the overall microplasma apparatus was identical to that of the DC-powered microplasma (Figure 2.3), except that the power supply was replaced with a high voltage, high frequency AC source and the supply gas was He which is generally easier to ignite than Ar.[134] The plasma was operated at 1.5 kV AC peak-to-peak voltage and a frequency of 35 KHz (PVM 500, Information Unlimited) in all experiments. Current though the circuit was measured using a toroidal induction probe (Pearson probe, model 2877) connected to the grounding wire and a 2 GHz oscilloscope.
Figure 3.2. Comparative circuit diagram of (a) DC and (b) AC microplasma apparatus. In both cases, the capillary was connected to the high voltage electrode and the substrate was grounded.

In order to improve the electrical performance of the films under applied strain, the films were prestrained during microplasma treatment. Prestraining is a technique in flexible electronics technology to preserve the conductivity of the conductive layer and make it less susceptible to
mechanical failure up to a higher applied strain. Figure 3.3 shows a flow diagram comparing films processed by the microplasma with and without prestrain. PDMS is a flexible substrate that allows us to strain it, even when coated with plasticized Ag-PAA. So we mounted the Ag-PAA films coated on PDMS on a 1D custom built micrometer stage. The 1D stage not only allows us to strain the sample by a specific amount, but provide electrical access points for the ground connection to enable patterning of the sample under strain.

![Flow Diagram of Film Preparation](image)

**Figure 3.3.** Flow diagram of film preparation for microplasma patterning without (top right) and with prestrain (bottom right)

### 3.2.4. Characterization and metrology

The microplasma-treated films were dried for 24 hours in a vacuum desiccator before electrical measurements. Two-point probe I-V measurements were carried out on a probe station using a Keithley Picoammeter (model 6485), Agilent ±25 V power supply (E3631A), and a custom
LabView program. Strain was applied uniaxially with a manual micrometer setup. A standard measure of electrical performance of thin metal films is bulk resistivity which is related to the geometry and measured resistance by the following:

$$R = \rho \frac{L}{A} \quad (2.1)$$

where $\rho$ is the bulk resistivity, $L$ is the length of the feature, and $A$ is the cross-sectional area of the feature width of 300 µm. When an elastic material is strained, it is deformed under compressive stresses perpendicular to it and $L$ and $A$ change (typically $L$ increases and $A$ decreases because the width correspondingly decreases), as illustrated in Figure 3.4, making it difficult to estimate resistivities. For this reason, the electrical characteristics of films under applied strain are usually related by a normalized resistance, $\frac{R}{R_0}$, where $R$ is the resistance of a feature measured from the I-V characteristics at a given applied strain (>0%) and $R_0$ is the resistance of the same feature measured from the I-V characteristics at 0% strain. The applied strain for the case of uniaxial strain was calculated as $\frac{\Delta L}{L_0} \times 100$, where $\Delta L$ is the relative change in length of the film and $L_0$ is the length of the unstrained film.
SEM and EDX measurements of AC microplasma-treated films were performed using FEI Quanta environmental SEM. Cross-sectional analysis of the films was performed using the methodology previously described in Section 2.2.3. SEM analysis was also performed in situ while the films were under applied strain. In this case, the features were manually strained by a desired amount and then mounted under the microscope. In order to preserve the precise surface morphology, the samples were not pre-coated with any conductive metal and were analyzed under an environmental SEM (ESEM, FEI Quanta) at a relatively high chamber pressure ($10^{-3}$ mTorr) in the presence of water vapor.

### 3.3. Results and discussion

When Ag-PAA-PDMS film stacks were exposed to the AC microplasma, highly reflective, white-gray features were immediately formed as the microplasma interacted with the film surface,
indicating reduction of Ag\textsuperscript{+} to metallic Ag [Figure 3.5(a)]. The crystallinity of the generated patterns was confirmed using X-ray diffraction (XRD) [Figure 3.5(b)]. The film stack could be mechanically released (peeled) from the electrode to obtain a free-standing [Figure 3.5(c), left], stretchable material [Figure 3.5(c), right].

Figure 3.5. (a) Optical image of an Ag pattern drawn on PDMS using AC helium jet microplasma, (b) XRD profiles of films analyzed before and after microplasma patterning, (c) Optical image of a patterned Ag-PAA film on PDMS peeled off from the anode (left) and stretched (right).
SEM analysis was carried out on a representative line array pattern to characterize the features produced by microplasma treatment of the Ag-PAA films on top of PDMS (Figure 3.6). The low magnification image shows that the line widths are ~300 μm [Figure 3.6(a)]. The pattern size is consistent with the microplasma diameter at the film surface which is larger than the capillary diameter of 180 μm because of gas expansion. The reduction process appears to be uniform across the line and produces high edge acuity. At higher magnification, an image of a region within one of the lines reveals that the reduced Ag layer is wrinkled at the surface [Figure 3.6(b)]. Wrinkle formation has been observed in thin metal films on polymer substrates because of compressive stress created by strain mismatch between the dissimilar materials.[135] Typically, wrinkling occurs during a thermal cycle where the stress is relieved and the metal buckles upon cooling.[136] Here, the films were not externally heated, although the plasma could locally heat the film, and the metal pattern was not deposited on top of the polymer, but instead was formed from inside it. It is possible that compressive stresses arose from either cooling as the plasma moved away or the diffusion-based process associated with metal layer formation. We note that after wrinkling, the films did not delaminate due to buckling,[137] and that all of this occurs despite the fact that the writing process is performed at a relatively rapid rate.
**Figure 3.6.** SEM analysis of metallic Ag patterns created by microplasma reduction of Ag-PAA films on PDMS: (a) low magnification image of array of lines, (b) high magnification image inside one of the lines, (c) cross-sectional image of a film section outside the line, (d) cross-sectional image of a film section inside one of the lines.

Cross-sectional images of the film outside [Figure 3.6(c)] and inside [Figure 3.6(d)] a patterned area indicate that the Ag is formed over a relatively thin layer near the surface of the film, with little change to the underlying region. Further, semi-quantitative analysis of the film was
done through energy-dispersive X-ray spectroscopy (EDX) based line scan of the films’ cross-section. Figure 3.7 shows a cross-sectional intensity profile of Ag from the surface to the bulk of the film. Representative SEM images (same scale as graph) are shown above and below the intensity plot. The EDX line scan confirms that the Ag concentration is enriched in a near surface region that is ~5 μm thick.
Figure 3.7. EDX cross-sectional line profile of a patterned region (image on top) and an un-patterned region (image below plot). The plots and the images are to scale.
The results for the AC microplasma treatment suggest that the reduction process is confined to the near surface region, similar to the DC microplasma (Section 2.3), and, again, Ag\(^+\) electrodiffusion is important. However, in comparison to a DC field, the electric field gradient across the film arising from an AC field at the surface switches polarity with time and it is not obvious how positively charged cations will have a net drift to the surface. We propose that there are several factors behind how this occurs. First, the reduction of Ag\(^+\) at the surface to Ag\(^0\) will lead to a concentration gradient that has been previously observed even for chemical reduction where no electric fields are present.[138] Second, as the electrically charged Ag\(^+\) is converted to the electrically neutral Ag\(^0\) (or small Ag clusters or nanoparticles), the surface potential will change. In particular, nanoparticles have been shown to cause perturbations to an AC field.[139,140,141,142] The perturbations can lead to surface polarization and net drift of Ag\(^+\) to the surface, which has also been termed rectification or anomalous current.[143]

The electrical properties of the microplasma reduced Ag-PAA films on PDMS were assessed as a function of strain by current-voltage (I-V) measurements using a 2-point probe method. The samples were uniaxially deformed and the I-V characteristics were measured in the same direction as the deformation. I-V characteristics representative of a 15 x 0.3 mm line on a 30 \(\mu\)m thick film containing Ag\(^+\):[COOH]\(^-\) = 0.45 are shown in Figure 3.8(a) and found to be highly linear as it was strained from 0 to 20\%. The increase in slope is indicative of an increase in the resistance. A linear I-V response was similarly found for films with other Ag\(^+\):[COOH]\(^-\) concentrations and thicknesses [Figures 3.8(b) and 3.8(c)]. From the I-V measurements, the average resistance, \(R\), was obtained and the normalized resistance, \(R/R_0\) was estimated where \(R_0\) is the average resistance of the film at 0\% strain. Figures 3.8(b) and 3.8(c) show that the normalized
resistance increases slowly up to a strain of ~10% (at 10% strain, $R/R_0$ has only increased by a factor of 10). This is observed in all films irrespective of their Ag precursor concentration and film thickness (>20 µm), which is in contrast to typical results for nanocomposites where the electrical properties are closely tied to the conductive filler concentration[144] and nanoparticle inks for direct-write printing where the amount of polymer encapsulation and the nanoparticle density and diameter dictate stretchability.[145] These results indicate that the microplasma reduction process does not strongly depend on the intrinsic properties of the film, perhaps because ionic diffusion dominates and always leads to a reduced Ag layer at the surface.
Figure 3.8. (a) I-V characteristics of 15 x 0.3 mm long features drawn on unstrained films with AC microplasma as a function of strain, (b) Normalized resistance ratio as a function of applied strain on (b) 80 µm thick Ag-PAA films of varying Ag concentration, and (c) films with Ag:PAA = 0.45 with varying film thickness.

The increase in resistance can be further understood from the microstructural evolution of the features under applied strain. Figure 3.9 shows the surface morphology of the features with increasing strain. Figure 3.9(a) and 3.9(b) are low and high magnification images, respectively, of a feature strained to 17% revealing homogeneous development of microcracks throughout the surface. Figure 3.9(c) and 3.9(d) are low and high magnification images, respectively, of the same pattern when strained to 35% and show that the cracks grow.
**Figure 3.9.** SEM images of Ag patterns created by microplasma reduction of Ag-PAA films under strain: (a) low and (b) high magnification images of a line strained to 17%, (c) low and (d) high magnification images of a line strained to 35%.

Together, the electrical characterization and SEM analysis show that when the microplasma-reduced features in Ag-PAA-PDMS films are strained, microcracks arise that are homogeneously distributed throughout the surface of the structure. At small strains less than ~17%, this only leads to a small change in resistance both because the cracks are small and because of the presence of wrinkles that had formed at the film surface during microplasma exposure and alleviate some of the film stress by aligning along the direction of the applied strain. As the applied strain is increased to 35%, the microcracks grow in size which probably leads to the loss of electrical continuity and larger change in resistance. Overall, the uniform crack formation and propagation indicate that the films exhibit strain dislocation, details of which will be explained in a later section of this chapter.

The morphology of the reduced Ag layer is found to be dramatically altered when the film is prestrained. Figure 3.10(a) shows a low magnification image of a line patterned at a prestrain of 27%. The lines are associated with local creases that extend to the neighboring unpatterned regions. At high magnification [Figure 3.10(b)] the features are characterized by Ag islands that are densely packed. Figure 3.10(c) shows a low magnification image of a similar Ag-PAA film that is patterned at a higher prestrain of 33%. These features appear to have a higher amount of buckling when released after patterning. At higher magnification [Figure 3.10(d)], the feature exhibits a high degree of packing to the point that the Ag islands are stacked on top of one another. Since these films were reduced by the microplasma while under tension and then released, it is clear that the reduced Ag is being compressed as the film relaxes to densify the Ag layer. Cracking
of the film is also observed, an indication of the compressive stress and resulting stress relief in the film [Figure 3.10(b)].

Figure 3.10. SEM images of Ag patterns created by microplasma reduction of patterned Ag-PAA films: (a) low and (b) high magnification images of a line patterned at prestrain of 27%, (c) low and (d) high magnification images of a line patterned at prestrain of 33%.
Prestraining was found to have a strong effect on the IV characteristics of the features when strained. Figure 3.11(a) shows the I-V characteristics of films that were prestained and stretched by 27% before patterning. It shows that the resistance (slope of the I-V plot) of the films increase as they are strained, with the highest resistance (lowest slope) occurring at 20% applied strain. Similarly, when the films are prestrained by 33% the I-V curves [Figure 3.11(b)] show a similar behavior. However, for the given voltage and applied train, the current passing through the circuit is higher than that observed from 27% prestrained films [Figure 3.11(a)]. The plot in Figure 3.11(b) also shows that with increasing strain, the resistance increases. However, in comparison to Figure 3.11(a), the base resistance $R_0$ and the strained resistance at 20% strain is much lower for 33% prestrained films. These differences become more clear from the normalized resistance which shows that the relative rate of change of resistance with strain. Figure 3.11(c) shows the relative change in the normalized resistance for films that were patterned under different amounts of prestrain. The solid dots in the figure represent the straining cycle and the hollow dots show the relative change of $R/R_0$ during the relaxation or relief cycle. The figure shows that when the Ag-PAA films are patterned under 0% strain, the normalized resistance starts to increase exponentially and reaches $R/R_0$ value of approximately 70 at only 17–18% strain. In comparison when the films are prestrained to 27% and 33%, $R/R_0$ increases to <10 up to 25 and 35% applied strain respectively.
Figure 3.11. IV characteristics of AC microplasma patterned 15 x 0.3 mm features on films that were prestrained to (a) 27% and (b) 33%, (c) R/R₀ of prestrained films. Solid dots represent average R/R₀ during straining cycle and hollow dots represent that measured during relaxation cycle. R/R₀ for a sputtered Au film on PDMS is included for reference; (d) Optical images of intensity of an LED connecting two lines patterned at 33% pre-strain with increasing strain.

For reference, we compared these results to a thin film of Au sputtered onto PDMS, stretched and electrically characterized on the same setup. The sputtered Au could only be strained to ~3% before R/R₀ showed a sharp increase. In addition, while conduction could not be restored
in the sputtered Au after straining, all of the microplasma reduced Ag-PAA films on PDMS, with and without prestrain, showed fully reversible conduction during a stretching cycle [hollow dots in Figure 3.11(c)]. The importance of our stretchability results is visually highlighted by Figure 3.11(d) which shows optical images of a LED chip electrically wired by the microplasma reduction of a film prestrained to 33%. The film is capable of being strained to 45% with only negligible decrease in the brightness presumably due to an increase in the resistance and a corresponding decrease in power delivered.

To understand the electrical performance of the microplasma-reduced prestrained Ag-PAA films on PDMS, we carried out SEM analysis of the films after applying strain and compared them to the morphology of the prestrained patterns at no strain (Figure 3.10). Figure 3.12 shows SEM images of features that were patterned at 27% and 33% prestrain and then analyzed under the microscope at different strains. Figures 3.12(a) and 3.12(b) are low and high magnification images respectively of features prestrained to 27% and then analyzed under the microscope at 17% applied strain. The high magnification image resembles the surface morphology of closely packed islands. Figures 3.12(c) and 3.12(d) are low and high magnification images of the same features at an applied strain of 35%. The high magnification image shows that at a strain of 35%, microcracks originate along the surface of the feature and are perpendicular to the direction of the applied strain. Figures 3.12(e) and 3.12(f) are low and high magnification images respectively of features patterned at a prestrain of 33% and then strained to 17% during SEM analysis. The high magnification image shows that the surface of the feature consists of large islands that are percolated with each other, thereby maintaining mechanical contact. Figures 3.12(g) and 3.12(h) shows the surface morphology of the same features when the applied strain is increased to 35%. The high magnification image shows that the previously formed islands now fit one beside another,
still maintaining physical contact and do not appear to sustain any microcracks. These results are consistent with the electrical measurements that showed small resistance change in these films when strained to the prestrain value.
Figure 3.12. SEM analysis of Ag patterns created by microplasma reduction of Ag-PAA films under strain: (a) low and (b) high magnification images of a line in a 27% prestrained film strained to 17%, (c) low and (d) high magnification images of a line in a 27% prestrained film strained to 35%, (e) low and (f) high magnification images of a line in a 33% prestrained film strained to 17%, (g) low and (h) high magnification images a line in a 33% prestrained film strained to 35%.

The above results can be explained as follows. When the patterns are fabricated under the microplasma at no prestrain, wrinkles form to alleviate the surface stresses due to thermal contraction. When these features are strained, the wrinkles align along the direction of the applied strain. On increasing the strain to >10%, microcracks begin to appear and they propagate with increasing strain and resistance increases. These observations indicate that there is strain delocalization in our films.\[146\] Strain delocalization usually requires strong adhesion between the different layers, for example the metal and polymer. Evidence in support of strong adhesion in our films is that the conductive metal features do not delaminate from the polymer surface when the film is strained. When the features are prepared under prestrain, the surface morphology indicates that the metallic region contains percolated large grains adjoining each other (see Figure 3.10). Thus, microcrack formation is delayed to higher strains and the films can be strained up to at least the prestrain value with only a small change in the resistance These observations are in stark contrast to metallic films deposited by conventional methods onto prestrained substrates where poor adhesion leads to strain localization and large crack formation.\[147\]

One of the most commonly accepted model for metal delamination from polymer substrates is due to strain localization.\[148\] The model proposed by Vlasaak et al. and illustrated in Figure 3.13(a) shows that when a metal is deposited on a polymer surface, there are local defects
that produce stresses at the metal-polymer interface. When strain is applied, these stresses are relieved by delamination and cracking of the metal from the polymer. To support our idea that AC microplasma patterned films exhibit strain delocalization and strong adhesion, we mounted one of our films under a strain of 35% and focus ion beamed (FIB) a region containing two surface cracks. Figure 3.13(b) shows the SEM image of this region after FIB milling. The demarcated area in white is zoomed in Figure 3.13(c) and a false color EDX map of this area is shown in Figure 3.13(d). These images reveal that there is no delamination between the top metallized layer and the bottom polymer layer due to the applied strain, in support of good adhesion. While our films show crack formation, we do not find any plastic deformation or delamination. Further, the metallized surface layer suffers from multiple cracks that are uniformly distributed throughout the area rather than localized crack propagation.[148] These results show that the AC microplasma process can be utilized to fabricate stretchable metallized layers on the surface of a polymer with efficient strain delocalization.
Figure 3.13. (a) Schematic representation of strain localization proposed by Vlasak[148], (b) SEM image of a patterned film strained to 35%, (c) high magnification image of a FIB-ed area highlighted in (a) and (c) EDX false color image of silver distribution in region shown in (b)

One might argue that FIB produces local heating effects and this might weld the surface Ag layer with the base and seal the cracks. Therefore, further quantification of the adhesion was performed using ASTM standard D3359, otherwise known as the scotch tape test. Results of this test is shown in Figure 3.14. Figure 3.14 (a) shows the image of an as-patterned film and Figure 3.14(b) is the image of the same film with scotch tape adhered to the top surface and then pressed uniformly with an eraser to ensure homogeneous adhesion. Figure 3.14(c) shows the image of the film after the adhesion test (left) and the adhesive side of the scotch tape after peeling it off the microplasma patterned Ag-PAA on PDMS film (right). It shows that after peeling the scotch tape from the patterns, only a very small amount of material can be observed on the scotch tape. By the ASTM scale, this was judged to be a 5 which corresponds to less than 1% removal of the original material after the scotch tape test. This provides further evidence that the films have good adhesion to the polymer and the stress incurred due to tensile straining of the films during stretching is delocalized uniformly.
Figure 3.14. Peel test of Ag-PAA on PDMS. (a) As-patterned sample of Ag-PAA on PDMS, (b) Sample with scotch tape pasted on top, (c) optical images of sample (left) and adhesive side of scotch tape (right) after peel test.

3.4. Summary

In summary, a microplasma process has been developed to pattern stretchable, electrically conductive metal features. The process is based on an AC microplasma which can be formed at the surface of thick insulating polymer films, and integrating the Ag-PAA chemistry with an
elastomer, PDMS. The advantages of our strategy over other approaches include the room
temperature and pressure operation, rapid direct-writing capability (500 μm/s), compatibility with
prestraining strategies, and independence from precursor concentration and film thickness.
Because the electrically conductive metal is produced from precursor cations within the film, the
adhesion is naturally created and helps delocalize the strain. The process is generic and should be
applicable to other metals and polymers, as well as non-planar substrates.
<table>
<thead>
<tr>
<th>Film preparation</th>
<th>Resistance (Ω)</th>
<th>Bulk Resistivity (mΩ-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration Ag⁺:[COOH]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>122</td>
<td>1.22</td>
</tr>
<tr>
<td>0.45</td>
<td>160</td>
<td>1.6</td>
</tr>
<tr>
<td>0.6</td>
<td>142</td>
<td>1.42</td>
</tr>
<tr>
<td>Film thickness (µm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>160</td>
<td>1.6</td>
</tr>
<tr>
<td>30</td>
<td>168</td>
<td>1.68</td>
</tr>
<tr>
<td>80</td>
<td>142</td>
<td>1.42</td>
</tr>
<tr>
<td>Film drying time after patterning (hrs)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>142</td>
<td>1.42</td>
</tr>
<tr>
<td>48</td>
<td>199</td>
<td>1.99</td>
</tr>
<tr>
<td>72</td>
<td>535</td>
<td>5.35</td>
</tr>
<tr>
<td>Pre-strain (%)</td>
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</tr>
<tr>
<td>0</td>
<td>168</td>
<td>1.68</td>
</tr>
<tr>
<td>26.67</td>
<td>103</td>
<td>1.03</td>
</tr>
<tr>
<td>33.33</td>
<td>93</td>
<td>0.93</td>
</tr>
<tr>
<td>Sputtered gold</td>
<td>47</td>
<td>0.47</td>
</tr>
</tbody>
</table>

**Table 3.1.** Specific resistivities of as-patterned features at 0% strain. Unless specified, all films contained Ag⁺:[COOH] = 0.45, >50 µm thick, dried for 24 hrs and patterned with 15 mm long lines that were 300 µm wide.
Chapter 4

Correlating plasma properties with nanoparticle reduction in metal-cation containing polymer

4.1. Introduction

While successful demonstration of plasma reduction of metal-cation containing polymers consisting of silver cations (Ag\(^+\)) and polyacrylic acid (PAA) has been shown, the exact mechanism for the reduction remains unclear. We have proposed an electrodiffusion model to some of the dependencies of the reduction such as the film thickness, plasma scan rate, extent of film drying, and the electrode geometry, but none of these effects clarifies how exactly the Ag\(^+\) is reduced by the plasma. This question is not only relevant in our studies, but is also becoming more broad as the synthesis of nanoparticles dispersed in thin films by a plasma process is emerging for a number of applications. In fact, the reduction of metal ions has been demonstrated at range of plasma conditions including low and high pressure (up to atmospheric), in a number of background gases, and with different plasma power couplings.[149,150,151,152,153]

In this chapter, we attempt to address the mechanistic questions by carrying out more careful experiments with two different plasma sources that have the capability to be controlled in terms of the charge flux to the surface. Previous studies have shown that photons are not responsible for the reduction of the metal cations and blocking the charge to the surface eliminates the reduction; therefore, controlling the charge flux is critical to understanding the reduction process. The first source that was employed is an extension of the direct-current microplasma presented in Chapter 2, except that in this case, charged particles are extracted by an additional electrode to create a secondary discharge. After exposing Ag-PAA films, the reduction was assessed by EDX intensity. Although this experiment does not rule out the effects of neutral
species such as Ar metastable states, the correlation of the reduction with charge flux suggests that charge species such as electrons are responsible. The second source that was employed is an electron-beam (e-beam) generated plasma produced in a low-pressure (25 – 100 mTorr) argon (Ar) background. Although this system is quite a bit different than the atmospheric-pressure microplasmas, it has several attributes that make it well-suited to study the mechanism behind plasma reduction of metal-cation containing polymers. A controlled operating background such as low pressure Ar eliminates the presence of chemically active species produced from ambient air (e.g., hydrogen radicals, H·) that could potentially play a role in reducing metal ions. In addition, these sources are characterized by a very low electron temperature [154] which limits the energy of excited species available compared to typical discharges [155], leading to a processing environment dominated by large fluxes of very low energy Ar ions (Ar+) or electrons.[156] Finally, the e-beam can be pulsed and so, in addition to process time and pressure, the pulse duration and pulse width are tunable to influence the plasma properties and thus flux of charged species to the polymer surface to further understand how reduction takes place. In this case, the reduction of Ag+ was characterized by ultraviolet-visible (UV-vis) absorbance spectroscopy which shows the localized surface plasmon resonance (LSPR) for the Ag nanoparticles that are formed. Quantitative analysis of the absorbance peaks allows an estimate of nanoparticle density in the films which we correlate with plasma properties to reveal that the flux of charged species controls the reduction and particle formation process in the film. While the specific role of ions and electrons could not be untangled, these results show the clear importance of charged species in plasma reduction of metal-cation containing polymers which could serve as a guide for future applications and fundamental studies.
4.2. Experimental methods

4.2.1. Extracted secondary discharge

If an external voltage is applied to an electrode nearby a direct-current plasma, charged species of the opposite polarity can be accelerated (extracted). At sufficiently high voltages, enough charged species are extracted and created by collisions with the background gas to produce another discharge. We refer to this as the extracted secondary discharge (ESD), and not a plasma, because at low voltages and charge carrier densities, a sheath may not be fully formed. An illustration of the setup for generating an ESD is schematically shown in Figure 4.1(a). A stainless steel capillary tube with flowing Ar was connected to a negative high voltage supply through a 250 kΩ ballast resistor. The anode of the power supply was connected to a 500 Ω resistor and a stainless steel mesh in series. Current in the primary plasma circuit was calculated from the voltage drop across this resistor. In order to extract charged species from this primary plasma, a third electrode was placed parallel to and downstream of the anode mesh. In our experiments, the electrode was connected to a positive high voltage supply to extract the negatively-charged electrons at a distance of 1 cm. A voltage divider was connected in series with the third electrode to prevent arcing. A schematic diagram of the ESD circuit is shown in Figure 4.1(b). Current through the ESD was measured by the voltage drop across a 1 MΩ resistor. It is possible to operate the ESD under open atmosphere. However, air can diffuse into the discharge, particularly in the ESD where the Ar flow has expanded, and affect the plasma characteristics. Therefore, the complete apparatus was mounted inside a glove box that could be backfilled with a nearly pure Ar atmosphere.
Figure 4.1. (a) Schematic diagram of ESD reactor encased in a glove box providing Ar atmosphere, (b) voltage divider circuit diagram for measuring ESD current

4.2.2. E-beam generated collimated plasma

The large area plasma processing system (LAPPS) is a Naval Research Laboratory (NRL)-developed technology that employs magnetically-collimated, sheet-like e-beams to generate similarly sized plasma sheets for materials processing.[157,158] A schematic of the processing system used in this work is shown in Figure 4.2. The base configuration consisted of an e-beam source, slotted anode, termination anode, sample holder, and magnetic field coils. Typically, the e-beams were 1-3 kV with current densities of 1-5 mA/cm². Co-axial magnetic fields of 100-300 Gauss were used to collimate the e-beam and thus improve uniformity along its length [159]. These parameters were sufficient to produce uniform plasma sheets compatible with large-scale systems (≤ 1 m²) operating at low pressures (< 100 mTorr).
For results described here, the plasma processing system and its operation for the modification of polymers has been described in detail in other studies by S. G. Walton et al. [160,161,162] Briefly, the system vacuum was maintained by a 250 l/s turbo pump, with a base pressure $\sim 10^{-6}$ Torr. The operating pressure was achieved by introducing Ar (purity $>99.9999\%$) through the mass flow controllers and throttling the pumping speed with a manual gate valve. The e-beam was produced by applying a -2 kV pulse to a linear hollow cathode for a given duration (pulse width) and frequency. The emergent beam passed through a slot in a grounded anode, traversed the gas, and was then terminated at a second grounded anode located further downstream.
The e-beam volume between the two anodes defines the ionization source volume, with the dimensions set by the slot size (1×25 cm$^2$) and the anode-to-anode length (40 cm). Pulse widths varied between 1 and 4 ms and the time between pulses (period = 1/frequency) ranged between 5 and 20 ms. The duty factor is defined as the pulse width/period and was varied between 5 and 40%. A magnetic field of 150 Gauss was produced by a set of external coils. The samples were placed on a 10.2 cm diameter stage located 3.0 cm from the e-beam axis. The stage was ground and held at room temperature.

System operation and monitoring during processing was carried out using a custom Labview software package. In addition to cathode operation (process run time, duty factor, pulse duration), the routine captures time-dependent cathode voltage and current measurements at specified intervals during the process run. The traces were stored and summed together at the end of the processing run to produce an averaged cathode response for the given conditions. The voltage pulse was monitored by reading the voltage across a voltage divider, whereas the discharge current was measured using a wide-band current monitor (Pearson Electronics, Model #3972).

Plasma characterization involved two separate reactors. Gas-phase characterization to determine plasma density was performed in a system described in [163,164]. This system utilizes a cylindrical e-beam that runs continuously and Langmuir probes to determine plasma density. Ion flux measurements were carried out in a system that employs an energy-resolving mass spectrometer (Hiden Analytical Ltd, EQP 300) as described in [165,166] and, like the processing experiments, uses a sheet e-beam that is pulsed. Although there will be some differences between the two systems, the important physics are similar. All other conditions were nominally the same so that the general trends could be compared. Specifically, the cathode currents and either electron density or ion flux were measured as the Ar pressure was varied over a range of 30-100 mTorr.
4.2.3. Film preparation and characterization

Thin films were prepared from high molecular weight PAA (Mn = 1.25 MM, Sigma-Aldrich) and AgNO\textsubscript{3} (99.9% metals basis, Alfa Aesar) as-received without further purification. 0.4 g PAA was first dissolved in 100 mL solvent containing 1:3 v/v water and ethanol, followed by the addition of 0.42 g AgNO\textsubscript{3} dissolved in 3 mL of the same solvent mixture and vigorous stirring. Another 50 mL ethanol was then added to this mixture to ensure complete precipitation of the silver cation-containing PAA (Ag-PAA) chelate.\[167\] The solution was subsequently centrifuged at 21,000 G (Beckman Coulter, Allegra) and the supernatant was discarded. The recovered precipitate was homogenized with 1 mL of 4:13 v/v mixture of water and ethylene glycol and degassed in vacuum for 10 min to enable casting on glass slides by doctor’s blade. All films were measured to be 5 ± 2 µm after drying as measured by a stylus profilometer (KLA Tencor).

The ESD exposes a film over an area that spans an effective diameter of approximately 1 cm. Scanning the film ensures that the exposure is uniform since the ESD may not be homogeneous. In addition to scanning, we also fabricated insulating glass masks that would not interfere with the charged particles to restrict the exposure area to a well-defined area. The masks were fabricated from 1” x 1” x 0.016” glass microscope slides (Corning, Inc.) using a 400 nm 0.5 W laser (Oxford Lasers, A series) that could be focused to a diameter of 10 µm. Typical patterns consisted of an array of 10 x 0.2 mm rectangular holes.

After exposing Ag-PAA films under the ESD, the generated patterns were characterized by SEM and EDX (FEI Nova) to analyze and quantify the reduction through intensity mapping. EDX maps of the patterns were translated into 8-bit grayscale image that could be interpreted as a 3D intensity map via image manipulation using ImageJ software.
Ag-PAA thin films that were treated in the e-beam LAPPS reactor were not patterned, simply due to the fact that the LAPPS plasma is a large area collimated plasma ensuring uniform exposure throughout the film. Typically, the e-beam reactor induces a uniform and low nucleation rate that was validated by the transparency of the films after treatment. Therefore, the formation of nanoparticles after exposure to the plasma at a given process condition was characterized by UV-vis absorbance spectroscopy (Shimadzu Model 1800). The morphology and dispersion of the nanoparticle inside the film was also assessed by scanning electron microscopy (SEM) (FEI, Helios) without any conductive metal coating.

4.3. Results and discussion

4.3.1. Characterization of Extracted Secondary Discharge (ESD)

Optical images of the ESD in operation are shown in Figure 4.3. Figure 4.3(a) is an optical image of the gap between the metal anode mesh and the 3rd positively biased metal electrode, separated by 10 mm. When the applied voltage bias on the third electrode was increased, the current and the optical intensity of the ESD increased as can be seen from Figures 4.3(b)-(h). Current-voltage (I-V) characteristics of the ESD operated in open air with flowing Ar and closed Ar environment at atmospheric pressure are shown in Figure 4.3(i). When the ESD was operated in open air, there was no increase in current up to an applied voltage of 3 kV. On further increasing the voltage, there was a relatively sharp increase in current to 200 µA at 4.5 kV. In comparison, when the operating environment was changed to Ar, there was a relatively linear increase in the ESD current up to 4.5 kV before a sharp jump occurred, indicative of gas breakdown. These two results combined, show that when the ESD is operated in open air, it is susceptible to interference
from atmospheric species such as O₂, H₂O and N₂. This interference cause little to no current at voltages up to 3 kV. On further increasing the applied voltage, there was a sharp increase in current signifying gas breakdown in the secondary discharge. On the contrary, if the ESD was operated in Ar atmosphere, the linear increase in current up to 4.5 kV was associated with a homogeneous optical intensity distribution [Figures 4.3 (b)-(f)]. On increasing the applied voltage to beyond 4.5 kV, the current increased rapidly for very small changes in voltages. This was also followed with a bright streak in the optical images [Figures 4.3 (g) and (h)]. This is the characteristic behavior of gas breakdown and was avoided for reduction of Ag-PAA because of the potential for heating and sputtering the film.
Figure 4.3. (a) Optical image showing the 1 cm spacing between the anode mesh and metal plate 3rd electrode. Optical images of ESD operating at (b) 1 kV, 50 µA, (c) 2.3 kV, 150 µA, (d) 3 kV, 250 µA, (e) 4 kV, 350 µA, (f) 4.7 kV, 500 µA, (g) 5 kV, 650 µA, and (h) 5.2 kV, 1050 µA; (i) I-V characteristics of the ESD operated in open air and Ar atmosphere at an electrode spacing of 1 cm.

In the presence of the Ag-PAA films, the I-V characteristics were found to change. Figure 4.4 shows the I-V characteristics of the ESD with a Ag-PAA film placed on the 3rd electrode. The surface resistance of as-prepared Ag-PAA thin films was ~ MΩ. This provides as additional resistance in series to the circuit and is observed through the drop in current for the same applied voltage at the 3rd electrode in comparison to that of the bare electrode.
Figure 4.4. I-V characteristics of ESD when operated with a bare metal as 3\textsuperscript{rd} electrode and with a 20 µm thick Ag-PAA film on the 3\textsuperscript{rd} electrode respectively.

4.3.2. Characterization of Ag-PAA thin films patterned under the ESD

The ESD operates over a circular area of approximately 1 cm diameter in comparison to the microplasma which is ~ 300 µm. Therefore, in order to quantify the exposure over a specified area, insulating shadow masks were fabricated using laser micromachining. Figure 4.5(a) shows an image of a laser machined shadow mask fabricated on glass slides. Figure 4.5(b) shows an image of a pattern generated by exposing 20 µm thick Ag-PAA films to the ESD at a current of 500 µA for varying time. Figure 4.5(c) shows an SEM image of patterns generated by the scanning ESD at varying currents for a fixed total time of 1 min/cm\textsuperscript{2} and the corresponding EDX false color map of Ag intensity distribution is shown in Figure 4.5(d).
Figure 4.5. (a) optical image of a glass shadow mask prepared by laser micromachining with feature sizes of 5 x 0.2 mm; SEM images of patterns generated by the ESD under varying plasma exposure (b) time and (c) current, and (d) EDX false color map of Ag from the patterns shown in (c).

These images show that with increasing time, the size of the features increase. Further, this increase is not completely limited by the fact that the features of the shadow mask had a width of 200 µm. Similar behavior is observed when the current of the ESD was varied. With increasing current, the feature sizes increase for the same amount of exposure time. These data were further quantified through image analysis shown as follows.
Figure 4.6. False color intensity heat maps of patterns collected from EDX analysis over a constant area of 1 cm² and treated for 12 mins at ESD currents of (a) 50 µA, (b) 250 µA, (c) 400 µA and (d) 600 µA.

Figure 4.6 shows the intensity profile of the patterns exposed under the ESD at varying currents and a constant exposure time of 12 mins. It was found that at very low currents [Figure 4.6(a)], there is no appreciable change in pattern intensity with respect to the unpatterned areas. With increasing currents to 250 to 400 µA [Figure 4.6(b) and 4.6(c)] the intensity of the patterns increase, validated by the formation of high intensity mountain ridges and relatively darker valleys of unpatterned areas. On increasing the current further to 600 µA [Figure 4.6(d)], the baseline
intensity of the unpatterned region increases and is indicated by a shift to lighter colors (purple to pink and orange). This shows that at higher currents, the fidelity of the patterns cannot be maintained due to reduction occurring under the mask. This can potentially be attributed to the increase in incident charge density that leads to a higher degree of collisions near the surface and thereby leaching to the areas covered by the mask and reducing them.

Figure 4.7. False color intensity heat maps of patterns collected from EDX analysis over a constant area of 1 cm² and treated at ESD current of 400 µA for (a) 1 min, (b) 5 min, (c) 10 min and (d) 20 min.

Similar to changing current, we also measured the intensity profiles of the ESD reduced patterns at a constant current and varying lengths of time. The extrapolated false color 3D maps
from EDX imaging for these experiments are shown in Figure 4.7. For very short exposure time of 1 min [Figure 4.7(a)] at 400 µA, there was no appreciable difference found between the exposed and unexposed areas. Increasing the exposure to 5 and 10 mins [Figure 4.7(b) and 4.7(c)] increasing the intensity of the exposed areas. At a relatively long exposure time of 20 mins [Figure 4.7(d)] the patterns are distinctly visible with a relatively higher width in comparison to the ones exposed for 5 and 20 mins. However, the increase in width is not as pronounced as that observed at very high currents [Figure 4.6(d)]. These images show that increasing time increases the total amount of reaction at the surface of the films. However, if the exposure is done under moderate ESD currents such as 400 µA, the fidelity of the features can be preserved.

The amount of reduction induced by the ESD can safely be attributed to the total amount of charge impinging the surface of the film since the total charge is given by $Q = I \cdot t$ where $I$ and $t$ are current and time respectively. In our experiments, we are using a programmable stage that can be set for specific scan distance and speed. Therefore, the total charge impinging the surface of the film can be interpreted as follows:

$$Q = I \cdot t = I \cdot \frac{D}{S_r} = I \cdot \frac{T \cdot n \cdot d}{S_r}$$

(4.1)

Where $D = \text{total distance travelled}$, $S_r = \text{scan rate}$, $n = \text{No. of scans}$, $d = \text{distance travelled by stage for each scan}$ and $T = \text{total time required for n scans of distance d}$. This equation shows that the total reduction is dependent of two factors, namely the current and exposure time. Figure 4.8 shows the plots of the maximum intensity obtained from the EDX false color maps of samples exposed under various currents and time shown in Figures 4.6 and 4.7. The bottom axis of the graph (blue) is a plot of the maximum intensity correlated to the exposure time at a current of 400 µA. The top axis (red) is the plot of the maximum measured EDX intensity of the patterns exposed for 12 mins for varying ESD currents. It shows that there is relatively linear increase in intensity under low...
exposure times between 0 – 7.5 mins. On further increasing the exposure time, the averaged maximum intensity saturates near a mean gray value of 155. In comparison, with increasing current, the averaged maximum intensity keeps increasing for same amount of exposure time. However, as is validated from Figures 4.6, at higher currents a lower fidelity is observed in the generated patterns.

Figure 4.8. Plot of maximum intensity obtained from EDX mapping of ESD reduced Ag patterns after conversion of the false color maps to 8-bit grayscale images. The EDX maps were obtained from samples exposed to the ESD for varying times (blue) and current (red).
These observations show that the ESD can smoothly be operated in a controlled atmosphere. Although the Ar atmosphere does not have any reducing species, the charged species generated in the microplasma are translated to the substrate via the ESD and they can induce reaction at the surface of the Ag-PAA thin films. There are two primary parameters that can affect the reduction of Ag\(^{+}\) from the ESD, namely current and time. Among these two factors, it was found that current has a more profound effect on the reduction and the fidelity of the patterns. At a higher current, the features increase in size and in extreme cases, might merge with neighboring features. This effect can potentially be attributed to the increase in charge density at higher currents. With a higher charge density, the collisions between the charges increase, especially due to the fact that the experiments are done at atmospheric pressure where the mean free path of particles is very low. The increased collision, particularly those near the surface of the film increases the total reduction. Further, since the shadow mask covered surface of the film is otherwise non-conducting, the impinging excess charges dissipate to the nearby regions leading to reduction of Ag outside the edges of the shadow mask. This effect can be reduced and high fidelity structures can be obtained if the treatment is done at a lower current for a longer time. In this case, a low density of charged species hit the substrate per unit time and therefore, assuming the same reaction rate, the impinging charges get enough time to reduce Ag\(^{+}\) near the surface and dissipate and preserve the pattern fidelity.

From these observations, it can be concluded that the charge density and duration of exposure of the Ag-PAA films to the charges can affect the total amount of reduction. However, it cannot be interpreted as the only factors that affect reduction of Ag\(^{+}\). Based on the limitations of the design of the ESD apparatus, other factors such as ambient pressure, plasma power etc. cannot be analyzed using this technique. Therefore, we use an e-beam generated plasma that can be
operated under varying conditions of pressure, power, time and pulse conditions and thus, can precisely control the total charge flux onto the sample in real time.

4.3.3. **E-beam plasma processing and characterization**

To understand the plasma reduction and nanoparticle formation process from the LAPPs plasma reactor, we exposed Ag-PAA films to the e-beam generated plasma at different operating conditions which in turn corresponded to changes in the charge particle flux to the surface. Plasmas produced in a low-pressure Ar background lack the ability to drive reactive, gas-phase chemistry and so it is reasonable to argue that the charged particles play a major role in reduction. The relationship between charged particle production and their transport to the surface to the input parameters such as background pressure, pulse duration (duty cycle), and pulse width are discussed below. We later address the potential role of photons on reduction (via photoreduction).

High-energy e-beams used to generate the plasma in this work are extracted from a hollow cathode discharge. The cathode discharge current depends on the cathode geometry, applied voltage, and gas pressure. [168,169] A cylindrically and linearly shaped cathode were studied here separately. The cylindrical cathode was used for studying plasma diagnostics and the linear cathode was used for sample treatment. Figure 4.9 shows that the increase in discharge current with increasing pressure is similar for both geometries. The beam extraction efficiency (beam current/discharge current) is not known and will likely vary with operating pressure [170]. However, the beam current is expected to increase with discharge current. Therefore, although the cathode geometries are different, the resultant plasma properties can safely be assumed to be the same.
In typical discharges, secondary charged species are produced by a low energy distribution of plasma electrons ($T_e \approx$ few eV) that have been heated via an applied electric field to overcome the elastic and inelastic electron collisions that reduce their energy, such that some fraction of the resulting electron population is energetic enough to sustain the plasma through ionization. In contrast, species production in e-beam generated plasmas is largely due to high-energy beam electrons (~keV) and the rate of species production, $S_i$, via energetic electron beams can be written as,
\[ S_i = k J_b N_i \sigma_i \] (4.2)

where \( J_b \) is the beam current density, \( N_i \) is the number density of the parent molecule or atom, \( \sigma_i \) is the cross section for species production (for a given beam energy), and \( k \) is a proportionality coefficient. [154] There are several important implications gleaned from Eq. 4.2 that distinguish e-beam produced plasmas from other discharges. Relevant to this work is the fact that a given species will be produced in proportion to the neutral density (gas pressure) and beam current and, thus, an increase in pressure results in an increase in the plasma density (see Figure 4.9). One might expect the density to increase at a faster rate than the discharge current since the current also increases with pressure, but the fact that it does not, suggests a higher beam extraction efficiency at lower pressures.

In noble gases, the primary loss of charged particles is diffusion to the walls. [165, 171] This means the source term \( S_i \) determines not only the plasma density, \( n_e \), but also the flux, \( \Gamma_i \), to the walls. For sheet beams (planar geometry), the flux can be estimated using,

\[ \Gamma_i \cong D_a \cdot n_i / l , \] (4.3)

where \( D_a \) is the ambipolar diffusion coefficient, \( n_i = n_e \) is the ion density at the beam axis, and \( l \) is the distance to the wall.[160] Figure 2 shows that the flux scales with density, despite any differences in source geometry and beam operation. Broadly, the results confirm that a correlation exists between discharge current, plasma density, and ion flux. Two important points to note are that 1) the flux of ions and electrons leaving a plasma are equal and 2) the magnetic field causes a net ion flux radially and net electron flux axially [160]. Thus, over a wide variety of operating conditions, it is possible to use the measured cathode discharge current as a proxy for charged particle flux to a surface (in this case the polymer film).
Representative discharge voltage and current waveforms are shown in Figure 4.10, corresponding to conditions used to process Ag-PAA thin films. The current measured during the applied high-voltage pulse is proportional to the beam current. As seen earlier (Figure 4.9), the current varies strongly with pressure, but varies little with process time. The discharge current depends on duty factor or pulse width [Figure 4.10(b)] because of the pulse forming network [172] where, generally current falls as the duty factor increases.
Figure 4.10. Representative plots of current and voltage showing waveforms of the applied plasma power used for treating Ag-PAA thin films with varying (a) period, (b) Pulse Width, (c) duration of treatment and (d) background operating pressure.

To understand the processing results in this study, it is instructive to consider how the charged particle flux or number of ions/electrons delivered to the film surface changes with operating conditions. The total number of species produced during each run based on Eq. 4.2 can be written as

$$S_{iTot} = (k_b N_i \sigma_i) (PW/T) t_p, \quad (4.4)$$

where $PW$ is the pulse width, $T$ is the period and $t_p$ is the processing time. The total charge, $Q_{Total}$, is equivalent to the number of beam electrons per pulse summed over all pulses and is proportional to the integrated area of the current trace during the applied high voltage multiplied by the total number of pulses ($t_p/T$):

$$(J_b)(PW/T)t_p = Q_{Total} = k' (t_p/T) \int_0^{PW} I_{cathode} dt \quad (4.5)$$

Thus, the total number of ions/electrons delivered to the surface during a given processing run, which from the results above is proportional to the number of ions created, can be written as

$$\Gamma_{iTot} \propto S_{iTot} = (k N_i \sigma_i) Q_{Total} \quad (4.6)$$

Figure 4.11 shows $Q_{Total}$ calculated from Eq. 4.5 for all operating conditions. As expected, $Q_{Total}$ increases with increasing pressure since the discharge current increases, while $Q_{Total}$ increases with processing time since the beam is on longer. Although the discharge current tends to decrease with duty factor, $Q_{Total}$ is largely unchanged as a function of pulse width and period.
Figure 4.11. Calculated values of total charge impinging on the surface in the processing reactor, calculated using equation 4.5. The total current is evaluated by integrating the area under the current waveforms shown in Figure 4.10 for (a) processing time and background pressure and (b) period and pulse width of the applied waveform.

4.3.4. Reduction and nanoparticle formation

After exposing Ag-PAA thin films to the e-beam generated plasma at different operating conditions, the films were characterized by UV-vis absorbance spectroscopy. Ag nanoparticles support localized surface plasmons and exhibit a characteristic absorbance peak in the range of 350 – 420 nm depending on their size, shape and concentration.[173,174] Figure 4.12 shows the absorbance spectra of 5 µm thick 0.3 Ag-PAA thin films coated on glass and then exposed to the plasma under varying conditions of pressure, exposure time, period and pulse width. The dotted lines represent raw scanned data from each film and the bold lines for each corresponding color is the averaged spectra. Figure 4.12 (a) shows absorbance spectra of Ag-PAA thin films exposed to
the e-beam plasma at varying pressures which confirm the presence of the localized surface plasmon band resonance (LSPR) band corresponding to Ag nanoparticles. The peak intensity of the band is found to increase with a small shift from 435 to 455 nm as the operating pressure is increased from 30 to 100 mTorr. Similarly, Figure 4.12(b) shows that increasing exposure time from 2 to 8 min at a constant pressure of 85 mTorr also increases the peak intensity of the measured LSPR band, but with a concomitant small decrease in the peak wavelength. Beyond 8 min, the peak intensity was found to shift back towards longer wavelengths. Figures 4.12(c) and (d) show UV-vis absorbance spectra of processed thin films at varying period and pulse width of the pulsed e-beam, respectively. While increasing the period was found to affect the absorbance spectra by increasing the peak intensity and red-shifting the peak wavelength, no strong dependence was found for pulse width when the period is fixed at 10 ms.
Figure 4.12. (a) UV absorbance characteristics of Ag-PAA thin films exposed to the e-beam plasma at varying conditions of (a) background pressure of Ar, (b) exposure time, (c) period of the applied pulse and (d) pulse width or duty cycle of the applied pulsing waveform.

Assuming that the films were relatively uniform in thickness across each sample and between samples and there was minimal specular scattering from surface roughness, the changes in the absorbance spectra are described by the Lambert-Beer law

\[ A = \varepsilon cl \]  \hspace{1cm} (4.7)
where $c$ is the concentration, $l$ is the path length, and $\varepsilon$ is the molar absorptivity or the extinction coefficient. The extinction coefficient is unique to the material and for Ag nanoparticles, values have been reported by Paramelle et al. as a function of particle size [174]. Thus, it is possible to estimate the average particle size and particle concentration from the measured absorbance peak wavelength and intensity for each of the processed films. The product of particle concentration with Avogadro’s number yields number density of the particle, which is used here on for easier conceptualization and study the effects of the process parameters on particle formation in the polymer matrix.

Table 4.1 shows a summary of the average particle sizes and number densities, $n$, extracted from absorbance spectra collected from all the processed films. We find that changing plasma parameters such as operating pressure, exposure time, pulse width, and duty cycle of driving voltages do not appreciably affect the particle size. Over the parameter space studied, the particle size is found to vary between 65 to 80 nm, a range of ±10%. However, changes in particle number density are more profound, especially when plasma reduction is done at higher pressures and longer time. For example, the particle density increase by almost a factor of 2 (with almost no change in the particle size) as either the pressure or treatment time is increased. In comparison, altering the pulse width does not significantly affect the particle size or number density.
Table 4.1. List of values of average particle size calculated from the correlation of absorbance peak intensity and wavelength of Ag nanoparticles synthesized in the e-beam plasma under various parameters with the extinction coefficient through the Lamber-beer’s law. The list of extinction coefficients has been extrapolated from Paramelle et al. [174] and the calculation assumes that all particles are spherical.

We suggest the following to explain these results. At higher pressures, the number of available charged species that can interact with the polymer surface increases due to a higher
plasma density. This leads to a higher nucleation rate and thus contributing to increasing particle number density with increasing pressure. In comparison, the particle density increases with exposure time, initially exhibiting a decrease in particle size, then increasing particle size. At relatively small exposure times the Ag\(^+\) within a few nm of the surface of the film is reduced. The neighboring Ag\(^+\) agglomerates forming a low density particle distribution with an absorption peak corresponding to particles of 80 nm diameter. Being embedded in a polymer matrix and the absence of any external electric fields, particle migration through the bulk of the film is limited, inhibiting high degree of agglomeration. As exposure time is increased, the number of available nucleation sites decrease but the rate of nucleation does not. This produces a relatively smaller the average particle diameter. Further increase in the plasma exposure time increases the depth of interaction of the charged species with the film bulk, generating increased nucleation sites and thus allows increasing number density. The increase in interaction depth can be attributed to various factors such as polymer degradation and surface etching which has previously been observed in other reports.[175] This is in contrast to previous studies with a DC microplasma where Ag\(^+\) is able to electrodif fuse from the bulk, providing a near-infinite reservoir of precursor for particle nucleation and growth.[176] Similar behavior is observed on varying the period of the driving voltage pulses at a fixed duty cycle. With increasing period, the time-interval between two consecutive high-pulse increase. Therefore, the charge flux is relatively continuous during a smaller pulse-period leading to increased particle nucleation rate and density. We did not observe any significant dependence of particle size or particle number density under systematic variation of duty cycle of the pulses.

To further characterize the films and support the UV-vis absorbance analysis, we performed SEM. Representative SEM images are shown in Figure 4.13(a) and 4.13(b) in
secondary emission (SE) and back scattered (EBSD) mode, respectively, of Ag-PAA films exposed at 85 mTorr for 8 min at a period of 20 ms and pulse width of 2 ms. The average particle size was estimated by analysis of the SE images using ImageJ to be approximately 10 ± 10 nm which is significantly smaller than obtained from UV-vis absorbance analysis. We attribute the discrepancy to arise from either surface charge effects in SEM or the assumptions that were made in extinction coefficients of Ag nanoparticles. We note that in addition to the SEM characterization limitations, the as-formed particles are embedded inside the polymer and purely surface characterization technique such as SEM may be insufficient to provide an exact estimate of particle size; in comparison UV-vis absorbance samples particles through the bulk of the film and may provide a more comprehensive average of all the particles. While SE is a surface image, EBSD mode can provide a higher depth profile and provides a qualitative estimate of the density distribution of nanoparticles on the surface of the film. Analyzing Figure 4.13(b) with ImageJ, we obtained a nanoparticle surface coverage of 43%.
Figure 4.13. Representative SEM images of e-beam plasma reduced Ag nanoparticles at the surface of Ag-PAA thin films collected from (a) secondary electron imaging and (b) backscattered imaging.

4.3.5. Correlating plasma parameters with Ag$^+$ reduction

To date, the exact mechanism for plasma reduction of metal cations either in polymer films or other systems such as liquids remains unknown. Various species have been proposed to be responsible including electrons, radicals, and photons. The combination of a low-pressure Ar background and reduction in a film makes it unlikely that reducing radicals are responsible. An alternative theory that can potentially play a role is plasma-induced photo-reduction. To test this possibility, samples partially covered by quartz slides (transmission: 250 – 800 nm) [Figure 4.14(a)] were exposed to the plasma at 85 mTorr for 8 min using a pulse width of 2 ms and a 10 ms period. As shown in Figure 4.14(b), only the uncovered part of the sample was reduced as indicated by the color change in the film and the quartz slide covered segment remained transparent. Absorbance measurements confirmed that the covered segment was completely unreduced [Figure 4.14(c)]. These results show that photons alone cannot reduce the Ag-PAA thin
films. Therefore, the possible reduction pathways can only be explained through ion bombardment or electron-induced electrochemical reduction.

**Figure 4.14.** (a) Schematic diagram of sample preparation to cover half with UV transparent quartz slide and expose the remaining half to the plasma, (b) Image of the sample showing the quartz
covered section (top left), the exposed section (bottom left) and a comparison with an as-prepared film (right); (c) UV absorbance spectra of different section of the Ag-PAA film shown in (b).

It is not clear thus far if the reduction is specifically being carried out by electrons, ions or charged metastables. However, it is possible to track changes in the material (absorbance) as a function the number of charges delivered to the surface as determined from equation 4.6. These results are shown in figure 4.15. It is a plot of the particle number density obtained from the absorbance spectra and the corresponding particle concentration and plotted as a function of charged delivered to the system during the plasma cycle. Figure 4.15 shows that particle concentration increases with increasing flux. This is particularly true when changing pressure and processing time; not quite so when varying duty factor.
Figure 4.15. Plot of correlation between the predicted concentration of particles formed after plasma exposure with the total charge impinging at the substrate for each experimental parameter.

The change in total Q (Figure 4.11) is less dramatic when changing duty factor (± 30 %) compared to pressure (400%) and increasing process time (550%). Moreover, the timescales associated with changes in period and pulse width, plasma decay, surface charging, and migration in the bulk are comparable and might well produce effects that are difficult to separate. To better understand the influence of duty factor, it is instructive to consider the direct relationship between number density and the amount of time the plasma is off. As shown in Figure 4.15, the particle density is found to increase as the off-time increases. In effect, the number density decrease as the
duty factor increases. While these results may seem counter intuitive to the results for an increasing pressure and process time, it is important to note the difference between the total flux of species and their duration. The reasons for this effect are not clear but maybe related to surface processes including the aforementioned surface charging and migration within the material. Regardless, the results do suggest the reduction process benefits from a modulation of charge delivery at the surface.

Taken together the results clearly indicate the reduction process is driven by a flux of charged particles. It is not clear if ions or electrons are the primary driver although it is reasonable to assume electrons are needed to reduce the Ag$^+$ ions to Ag$^0$ nanoparticles.

4.4. Summary and conclusions

In summary, we have shown that a microplasma can be tuned with an external voltage bias to draw a relative small shower of charge that we term as microhollow cathode secondary discharge (ESD). ESD was found to be relatively stable without causing a secondary gas breakdown when operated in inert Ar atmosphere. The charge emanated from the ESD can be reduce Ag$^+$ to Ag$^0$ at the surface of a metal ion containing polymer such as PAA. The total amount of reduction can be tuned by controlling the exposure time and the ESD current. Current was found to have a more profound effect on the reduction and when patterning is desired, a longer exposure time at a lower current can produce patterns of higher fidelity.

In the second part of this chapter we have shown that e-beam generated plasma produced in low pressure argon background can reduce Ag$^+$ to Ag$^0$ nanoparticles. Further, we presented a systematic approach to analyze interactions of plasma-generated species with a metal-ion containing thin polymer films. The plasma interaction produces a high density of nanoparticles
embedded within the polymer matrix. The nanoparticle formation can be tuned by tailoring the operating pressure and exposure time. Variation of other plasma parameters such as period and duty cycle are found to have less profound effects on the nanoparticle formation.

From our analysis, it was found that the reduction of metal ions into nanoparticles by plasma exposure can depend on potentially a number of factors. However, the only species responsible for reducing Ag\(^{+}\) is sourced from the charged species in the plasma. The total amount of charged species impinging the substrate can be controlled by a number of different factors; the most significant of them being the plasma current, background pressure and exposure time. Subsequently, the number density of the nanoparticles embedded on the polymer can be tuned and controlled. Additionally, using a suite of plasma diagnostics, it was shown that plasma density and thus flux to the surface can be controlled using straightforward changes in operating conditions. By comparing the processing and plasmas diagnostic results, we find that as charge particle flux to the surface increases the Ag nanoparticle number density also increases. Through control experiments, it has been proven that photons are unable to reduce the metal ions. We thus conclude charge particle flux to the surface plays a dominant role in the reduction of Ag\(^{+}\) and subsequent nucleation of nanoparticles in this system. While charged particles are clearly important, the specific role of ions and electrons could not be determined. These results serve as a guide for ongoing studies, optimizing plasma parameters, and future applications for in \textit{in situ} formation of nanocomposite films by plasma reduction.
Chapter 5

Low-pressure plasma reduction of organic-free printed metal salt

5.1. Introduction

In the previous chapters described this far, we have shown how species generated from a plasma can reduce metal ions embedded in polymers. Depending on the plasma conditions and flux of the charged species, the total amount of reduction can be controlled. We have shown how three different plasmas, namely, DC and AC atmospheric-pressure microplasmas and an ebeam generated low-pressure plasma can effective produce similar results – reduce metal ions to metal nanoparticles. The DC and AC microplasmas are highly localized, but have relatively high density leading to a higher reduction, leading to percolation of the reduced nanoparticles and producing conductive features. The e-beam generated plasma on the other hand has a low charge density and exposure to Ag-PAA thin films to this results in well-dispersed nanoparticles that are homogeneously distributed throughout the surface of the film.

All of these methods shown so far had two primary components – silver precursor AgNO$_3$ was mixed with a stabilizing polymer PAA and cast as a smooth film. As we have seen so far, this singular film preparation technique is applicable for all three types of plasma systems. Although both conductivity and plasmonic characteristics are contributed from Ag nanoparticles, the presence of polymers can potentially inhibit particle reduction. In this chapter, we will show how this issue can be addressed without the use of any stabilizing polymer, yet conductive pattern can be generated using a low-pressure, low-temperature plasma. We demonstrate the fabrication of a particle-free, stabilizer free metal ion containing ink that can be printed and them plasma-treated
at room temperature. The plasma reduction is simultaneously accompanied by \textit{in situ} sintering to form highly conductive patterns. The physical properties of the ink such as surface tension and viscosity can be tailored to fit the requirement of any printed by simply modifying the volume of the components in the solvent mixture. Patterns were printed on scotch tape and then plasma reduced in Ar to fabricate electrically conductive structures. It was found that the Ar plasma treatment results in rapid reduction and sintering of the structures and subsequent control of resistivity. This technique of fabrication of metallic patterned thin film conductors provide us with a singular efficient method to control resistivity of the patterns depending on the application. As an application, we show that by tailoring the resistivity of the pattern we can control the cut-off frequency of a low-pass filter.

5.2. Experimental methods

5.2.1. Solution preparation and printing

AgNO$_3$ (98% purity, Alfa Aesar), Ethylene Glycol (Fisher Scientific) and Ethanol (200 proof, Fisher Scientific) were used as is without any further purification. 1.2 M AgNO$_3$ was measured for 20 ml solution and then dissolved in 3 ml ethanol and 1 ml DI water (Millipore). The resultant solution was then dissolved in ethylene glycol such that the measured viscosity (Brookfield DV-E) was between 10 – 12 cP. Following this, the surface tension of the solution was measured with a tensiometer (Kruss K100) such the recorded value was between 28 – 33 dynes/cm. More ethylene glycol or ethanol was added if necessary to achieve the requisite values of viscosity and surface tension. Usually, the total volume of the mixture and thus the stock ink solution was $20 \pm 1.5$ ml. This ink was used as is and was stored in the refrigerator.
All printing was performed with a Fujifilm Dimatix printer with 16 piezoelectric nozzles. Requisite patterns were preprogrammed and the drop sizes, spacing and nozzle driving waveforms could be tailored from the computer.

5.2.2. Plasma treatment

Plasma treatment was performed in a pure Ar (Purity 99.9999%, Air Gas) environment. The plasma chamber (Nordstorm March PX250) was connected to an external 600 W, 13.56 MHz RF power supply (ENI, ACG-6B-06). The input power, gas pressure and exposure time could be controlled directly from the plasma asher. Samples were placed on the grounding plate inside the chamber for all experimental consistency. The chamber was degassed to 60 mTorr and then purged with Ar for 10 mins before all experiments to ensure the absence of any foreign species. An optical image of the plasma chamber in operation is shown in Figure 5.1.

Figure 5.1. Optical image of the low-pressure 13.56 MHz plasma chamber in operation with Ar atmosphere
5.2.3. Characterization

I-V characterization was performed on a I-V station by a 2 probe method using a power supply (Agilent 34401A) and a picoammeter (Kiethley 6400) that were controlled from a custom LabView program. Data for each feature was collected over multiple lines to ensure accurate reproducibility through standard deviation. Crystallinity of the features were measured through XRD (Rigaku D/Max 2200). In order to ensure a clean background, samples for XRD were printed on glass slides instead of scotch tape. Surface analysis of the features were analyzed by profilometer (KLA Tencor) and scanning electron microscopy (FEI Nova).

5.2.4. Printing RC circuit and its plasma treatment

Various patterns of RC circuits were printed during the course of these experiments. Special care needed to be taken to avoid stray capacitances and inductance from coiled circuits. Examples of two different RC circuits is shown in Figure 5.2. In both cases repeated back and forth coiling of the resistive component led to excess stray capacitance and inductance from the circuit. The final test structure has is shown later in Section 5.3. The resistivity of the resistive component in the RC circuit was varied by varying the plasma exposure parameters such as time, power and pressure. After exposing the resistive component, it was masked with scotch tape and the capacitive component was exposed at 200 W, 20 mins at 650 mTorr to ensure minimum contribution towards resistance in the circuit from the capacitive electrodes. Frequency performance of the plasma treated RC circuits were measured by applying a nominal 5 V sinusoidal frequency to the circuit from a frequency generator. The output was measured through an oscilloscope. The RC performance and the cutoff frequency is measured by plotting the logarithmic ratio of the output and the input voltages and plotting against the applied frequency. The cutoff frequency is defined as the point where the output is -20 dB.
Figure 5.2. Representative optical images of two plasma reduced RC circuits that were not used as RC filters due to inductance and stray capacitance.

5.3. Results and discussions

Particle-free silver ink was prepared by a simple one-step process. Silver nitrate was dissolved in a mixture of ethanol and ethylene glycol and was printed using a Fujifilm Dimatix printer. The composition of solvent varied, depending on the surface tension and viscosity requirements of the printer nozzle. In our case, proper print could be obtained when the viscosity was between 10 – 12 cP and surface tension was 30 dynes/cm. AgNO₃ concentration in the solution
was fixed at 1.2 M. The printer bed was heated to 50°C to achieve consistency over all experiments and ensure efficient drying of the jetted droplets. Among the various factors that were found to have implications on the final resistance of the printed features, drop density and ambient humidity were critical to proper jetting.

Optical images of water contact angle of droplets printed on Epson photopaper™ and scotch tape (3M®) is shown in Figure 5.3. Figure 5.3(a) shows that the deposited ink is completely absorbed and the effective contact angle is zero. In comparison, when the ink is printed on scotch tape, it forms an acute angle at the junction between the scotch tape and the ink. When the ink is printed on the photopaper, its permeability and porous microstructure absorbs the ink into the fibrous bulk and therefore, minimal amount of salt is left at the surface of the paper. Plasma reduction of the patterns printed on photopaper did not yield high conductivity. In comparison, scotch tape is also hydrophilic, but not permeable. This allows the jetted ink to reside at the surface. Requisite patterns were therefore printed on commercial scotch tape.

Figure 5.3. Water contact angle measurements of AgNO₃ ink on (a) Epson photopaper and (b) Scotch tape.
The as-printed features were then placed under the plasma for varying treatment times. Figure 5.4 shows the morphology and appearance of the printed features. Figure 5.4(a) is a 3D scanned image obtained from a stylus profilometer, scanned over a representative 300 μm wide feature. When this image was further analyzed along the axis of the feature and averaged [Figure 5.4(a), right], it was found that the feature height and roughness varied between ±1.5 μm. When the surface profile was extrapolated perpendicular to the line axis [Figure 5.4(a), bottom], the step height of the printed feature was found to be approximately 5 μm. The background roughness of the scotch tape was ±1 μm. Figure 5.4(b) shows optical images of as-printed and plasma treated patterns. Before plasma treatment, the features appear near-transparent with a crystalline texture to naked eye. After plasma exposure, these features develop a shiny silvery color. These results show that the as-printed structures have a rigid morphology that is similar to precipitation of crystals observed during recrystallization for analytical chemistry.
Figure 5.4. (a) 3D scanned profile of a printed structure when analyzed under a stylus profilometer. The variation in average roughness perpendicular to the length of the feature is shown to the right of the image and the average step height of the printed feature with respect to the scotch-tape background is shown below the 3D scan. (b) optical images of a set of printed feature before (left and after (right) plasma treatment.
Confirmation of plasma reduction was found through X-ray diffraction (XRD) studies. Figure 5.5(a) shows XRD spectrum obtained from samples exposed to an Ar plasma at 200 W at a background pressure of 613 mTorr for varying lengths of time. It was found that with increasing exposure time there is a rise in crystallinity of the reduced features, validated by an increase in the peak intensity of metallic Ag. Simultaneously, the crystalline peaks corresponding to that of AgNO₃ reduce and finally disappear with increasing plasma exposure time. This shows that Ar plasma treatment of printed AgNO₃ structures results in situ reduction and agglomeration of Ag into crystalline metallic phase.
Figure 5.5. (a) X-Ray diffraction (XRD) spectra of printed AgNO3 structures and treated in an Ar plasma at 650 mTorr and 200 W applied RF power for varying durations, (b) I-V characteristics of as-printed patterns treated at 200 W plasma power at 650 mTorr for varying plasma durations.
In order to confirm the electrical continuity of the printed structures, we measured current-voltage (I-V) characteristics of lines that were 16 x 0.3 mm in size. Figure 5.5(b) shows the I-V characteristics of these features. The as-printed features were exposed to Ar plasma at 200 W and 650 mTorr operating pressure for varying lengths of time. It shows that with increasing exposure time the slope of the plots increase, which is indicative of a decrease in resistance. Figures 5.5(a) and 5.5(b) validate the picture that with increasing plasma exposure, more Ag\(^+\) ions in the pattern get reduced and therefore the crystallinity increases and simultaneously the resistivity decreases.

Similar studies were performed with varying pressure and plasma power. Figure 5.6(a) shows the I-V characteristics of similar features that were plasma exposed at 200 W for 20 mins for varying operating pressures. It shows that with increasing pressure and the same plasma exposure parameters, the slope of the graph increases, indicating that the resistance decreases. Figure 5.6(b) is a plot of the corresponding bulk resistivities of the same features, evaluated from the plot in Figure 5.6(a). It shows that with increasing background pressure the resistivity of the features decrease from 16 mΩ-cm to 0.7 mΩ-cm between operating pressures of 115 mTorr to 613 mTorr respectively. Similarly, two other plasma parameters, namely exposure time and plasma power were analyzed using the same methodology. Results of these parameters is shown through the change in resistivity in Figure 5.6(c). It shows that with increasing the plasma power from 50 W to 200 W, the resistivity of the features decrease. At a low power of 50 and 125 W and 1 min exposure time, the resistivity is 10 Ω-cm. In comparison the resistivity of the features when exposed for the same time at 200 W is 0.01 Ω-cm, a threefold decrease. With increasing exposure time to 5 mins, a higher power (200 W) results in a comparatively lower resistivity. On further increasing the exposure time to 20 mins or more, the resultant resistivity is independent of the applied plasma power. These results show that a longer exposure time and a higher applied
pressure is critical to attaining a lower resistivity. Further, resistance of the features is less dependent on the applied plasma power. It is worth noting that at a higher applied power and long exposure time, the surface temperature inside the plasma chamber increases. For highly temperature sensitive substrates such as most polymers, protocols being reported in this report can be followed by simply using longer exposure time and a low plasma power.
Figure 5.6. (a) I-V characteristics of 16 x 0.3 mm features that were treated for 20 mins at 200 W Ar plasma under varying operating pressures, (b) bulk resistivities of the features whose I-V characteristics has been shown in (a), and (c) plot showing the change in bulk resistivities of similar features exposed at 650 mTorr for varying time and plasma power.

Figure 5.7 shows SEM images of printed patterns. Figure 5.7(a) and 5.7(b) are low and high resolution images of as-printed patterns respectively. Figure 5.7(c) and 5.7(d) are low and high resolution images of the same patterns after plasma treatment respectively. The plasma treatment was done at 200 W for 20 mins at 613 mTorr. At low resolution, it was found that there was no change in surface morphology before and after plasma exposure [Figure 5.7(a) and Figure 5.7(c)]. Under high resolution, the surface of the features appears to have multiple flakes that are overlaid on top of each other before plasma exposure [Figure 5.7(b)]. After plasma treatment, these features converge into a single monolithic structure without any overlapping flakes [Figure 5.7(d)].
Figure 5.7. (a) Low resolution and (b) high resolution SEM images of as-printed features before plasma exposure, (c) low resolution and (d) high resolution SEM images of the same features after plasma exposure at 200 W for 20 mins under an operating pressure of 650 mTorr.

The above results can be explained as follows. Solutions of AgNO$_3$ can be printed using a piezoelectric nozzle such as the one in our Fujifilm Dimatix printer. Once jetted, the droplets dry to form crystals of AgNO$_3$ on the scotch tape. These crystals appear similar to those found in recrystallization methods used for salt purification, as is valid from the profilometry scan shown in Figure 5.4(a). When exposed to the plasma, Ag$^+$ in the crystals get reduced to Ag$^0$ at the surface.
of the crystals. On increasing the plasma exposure time, the depth of reduction increases and simultaneously the reduced Ag\(^0\) start to agglomerate into crystalline and percolated metallic macrostructures as is validated by the increase in crystallinity [Figure 5.5(a)] and the conductivity [Figure 5.5(b)]. On the other hand, we have also seen from Figure 5.6(a) that with increasing pressure the resistivity of the pattern decrease. We hypothesize that increasing the background pressure increases the density of the charged species in the plasma. Thus a larger number of electrons are available to induce electrochemical reduction of Ag\(^+\). Subsequently for the same exposure time, plasma treatment at a higher pressure leads to a lower bulk resistivity [Figure 5.6(b)]. In addition to factors such as exposure time and operating pressure, the other obvious knob that can control the resistivity of the features is the plasma power. Validated with the decrease in resistivity with time in Figure 5.6(c), we see that at a low applied plasma power of 50 W the resistivity of the features starts to decrease and then flatten out beyond 15 mins. Under the same exposure conditions, except a higher plasma power of 200 W, we see that the decrease in resistance is much more rapid and flattens at approximately 8 mins of exposure time. This shows that at a higher plasma power, the amount of reduction of the Ag\(^+\) is higher per unit time leading to a more rapid decrease in resistivity. Typically, interaction of charged species from a plasma is limited to the surface of a structure. Further, with longer exposure time and higher power, the depth of reduction increases and further, the macroscopic crystals of AgNO\(_3\) fuse to form a homogeneous and percolated electrically conducting features. Depending on the plasma exposure parameters, the resistivity of the features can be varied from that of non-conducting AgNO\(_3\) patterns down to 0.1 m\(\Omega\)-cm of plasma reduced conducting Ag patterns.

The ability to vary the resistivity of the patterns were employed in our work through the fabrication of low-band pass RC filter on scotch tape. An image of the printed and plasma reduced
RC pattern is shown in Figure 5.8(a). This particular design, owing to the high aspect ratio of the conductive features minimizes inductive loading of the circuit. We were thus able to measure the frequency performance of the circuit based on a purely resistance-capacitance model. Figure 5.8(b) shows the Bode plot of the RC filter. Bode plot represents the frequency performance of the RC filter. In each of the measurements, separate circuits were printed. The resistive component was exposed to a 125 W Ar plasma at 650 mTorr operating pressure for varying exposure duration, which tailors its resistivity. In order to ensure that no or minimal resistance to the circuit is contributed from the capacitive component, the resistor was masked with another scotch tape and the capacitor was then exposed to the Ar plasma at 200 W and 650 mTorr operating pressure for 20 min. After plasma exposure, a sinusoidal voltage of 5 V was applied across the circuit, after connecting the R and C components in series. The ratio of the output voltage with the 5 V input voltage is expressed as logarithmic noise (dB) and plotted as a function of the input frequency. This generates the Bode plot. We found that with increasing frequency, the output voltage decreases. However, the rate of decrease of the output voltage is higher for a circuit with higher resistance (low deration of plasma exposure) and relatively low for lower resistance (longer plasma exposure). This is an expected performance of the RC circuit, which is given by the formula

$$f_c = \frac{1}{2\pi RC},$$

where $f_c$ is the cut-off frequency defined as the frequency at a noise level of 20 dB per decade.
Figure 5.8. (a) Optical image of a representative RC filter used for the measurement of cut-off frequencies for each resistors, (b) Bode plot for RC filters shown in (a)
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