SOLID-STATE SUPERIONIC CONDUCTORS FOR ADVANCED
NANOSCALE FABRICATION

BY

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ABSTRACT

Silver possesses the highest electrical conductivity of any metal, and this property allows for unique interaction with visible light when patterned at the nanoscale. Few methods exist for patterning silver down to sub-100nm scales, and all tend to be complicated, multi-step processes which require expensive equipment. This work examines the use of the solid electrolyte glass silver iodide-silver metaphosphate (AgIAgPO$_3$) as a pathway for nanoscale patterning of silver using simple processing. AgIAgPO$_3$ was chosen as an ideal candidate solid ionic conductor because it is optically transparent, has a high ionic conductivity for silver at room temperature, and most importantly it has a remarkably low glass transition temperature which facilitates low temperature thermal nanoscale molding.

Our laboratory has previously developed a process known as solid-state superionic stamping (S4) to selectively etch silver and copper films by generating localized electrochemical metal etching using the patterned solid ionic conductor Ag$_2$S as a stamp, achieving sub-50nm lateral resolution. In this work, AgIAgPO$_3$ is developed as a replacement solid electrolyte with many superior properties to Ag$_2$S. The primary advancement is the use of thermal nanoinprint to manufacture large area stamps on the same system in which the S4 patterning is performed. This allows scalable, high quality stamp surfaces to be generated within minutes, without the need for difficult and contamination prone polishing.

Initially, a working AgIAgPO$_3$ prototype stamping process was generated with dimensions of 0.3-1mm, similar to that achievable with Ag$_2$S stamps. It was found that these stamps were capable of significantly higher etch rates due to the higher stamp ionic conductivity. Moreover, since AgIAgPO$_3$ is a pure ionic conductor—as opposed to Ag$_2$S, a mixed conductor—analysis of etch progression is possible through the measured charge transfer.

Continued investment into the S4 process involved developing a better
platform for the manufacture, handling, and application of S4 stamps by augmenting a 4-axis precision stage system to accommodate controlled and repeatable thermal nanoimprint for on-machine stamp fabrication. The system was designed for the precise temperature and pressure control needed to produce optically flat stamps suited to make large area contact between two hard materials. Once built, the system was modeled and characterized to determine which parameters in stamp fabrication had the greatest effect on the molding process. While some parameters such as the mold temperature primarily only effect the molding time, others such as the temperature of the stamp holder had a large effect on the overall curvature of the final stamp. This characterization leads to the ability to fabricate stamps with less than 200nm total curvature across a 4mm diameter of the stamp.

While working with AgIAgPO$_3$, the clarity needed for optically imaging through the material brought to the fore significant shortcomings in widely used glass synthesis techniques, typically brought about by the exchange of expensive of platinum crucibles for lower cost alternatives. Through chemical analysis, the identity of the contamination was determined and methods for either removing the impurities or avoiding their introduction were analyzed.

In contrast to controlling electrode-electrolyte contact at the nanoscale by patterning the electrolyte, nanoscale application of charge through electron beam irradiation was also explored. Localized injection of charge into the surface of the electrolyte, was found to precipitate silver nanoparticles within the interaction volume generated by the beam. Low electrical fluence results in the formation of a layer of embedded nanoparticles which produce vivid colors in reflected light. Meanwhile, at large fluence full silver films were formed, with lateral dimensions of the film determined by the electron beam path. Moreover, by varying the beam energy, it was possible to enter a regime that results in dissolution of the generated color, effectively allowing color patterns to be erased.

Finally, an effort was made to control, at the nanoscale, the bulk extraction of silver from the solid electrolyte. Attempts to laterally confine silver growth, and thus produce long wires, were unsuccessful despite the presence of insulating confinement layers. Much more effective, was pre-patterning of the glass surface with a low fluence from the electron beam prior to a higher current silver extraction via micro-probe on the glass surface. The presence of silver particles within the surface serve to accelerate the lateral growth of
silver films by up to 80 times that found in areas lacking the pre-pattern.
To my parents, for their love and support.
I would like to acknowledge my friends and coworkers within our lab. You have made it a pleasure to work here and I always know I can stop by to ask a silly question.

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CHAPTER 1
INTRODUCTION

Fabrication and patterning of metal structures is one of the primary technologies in microfabrication that enables the creation of complex electrical, chemical, and optical systems. Miniaturization enables systems such as integrated circuits to be produced cost effectively, with devices containing billions of transistors which need metal wires interconnecting them. Transistor dimensions in current processes are already at 14 nm, with those in industry attempting to keep up with Moores law which requires that transistors, and the wires that connect them, keep shrinking.[1] Although most integrated circuits use aluminum or copper interconnects, of all metals, silver possesses the highest electrical and thermal conductivities, allowing for the smallest resistive losses and highest heat transport out of devices.[2] Even when silver is not the end product desired, nano-patterned silver has proven essential in novel etching techniques such as metal assisted chemical etching, where a nano-pattened silver film is used as a catalyst for high aspect ratio etching of silicon.[3]

The high conductivity of silver is also responsible for silver’s high reflectivity within the visible wavelengths. In the more localized interaction of light along metal-dielectric interfaces, known as plasmonics, this leads to high quality resonance of nanoscale silver particles with visible light excitation. Localized surface plasmon resonance, as it is known, is finding numerous applications due to the greatly enhanced localized electric fields associated with sharp metal features. Silver particles are also being researched for light trapping in photovoltaics, light filtering, and chemical sensing at interfaces.[4, 5, 6, 7, 8, 9, 10]

The enhanced electric field around silver particles greatly enhances several processes that scale nonlinearly with the local electric field, including raman, fluorescence and infrared absorption, leading to the advanced chemical sensing techniques of surface enhanced raman spectroscopy (SERS), surf-
face enhanced fluorescence (SEF), and surface enhanced infrared absorption (SEIRA).\cite{10}\] In particular, the raman signal obtained from molecules near a nanoscale patterned metal surface can be enhanced by up to $10^5\text{-}10^8$ over a regular substrate.\cite{8}

### 1.1 Metal Nanopatterning Techniques

Scaling metal patterning down to nanometer length is difficult for traditional microfabrication especially for large volume, flexible pattern applications. By far, the most common and economical technique for metal patterning is a combination of photolithography, metal deposition, and lift-off. In one variant of this method shown in Figure 1.1, a photosensitive polymer photoresist is spun onto a substrate. The polymer is then exposed to ultraviolet (UV) light though an opaque mask, causing portions of the photoresist to undergo a chemical reaction which either increases or decreases the polymer’s solubility in developer solutions. This permits selective dissolution of the photoresist in a development process (whether the UV exposed portion is removed or remains depends on the type of resist), exposing a portion of the substrate while covering other areas. Metal deposition can then occur through metal evaporation or sputtering to coat the entire substrate. Finally, the remaining photoresist is dissolved and lifts off the metal that was not directly in contact with the underlying substrate.

The benefit of traditional photolithography is that the pattern-defining UV exposure can be applied over an entire wafer at once, resulting in high overall throughput. However, in photolithography the feature resolution is limited by both the wavelength of light used, and the resist thickness as shown with equation 1.1 showing the resolution limit for a contact-based process.

\[
R = \frac{3}{2} \sqrt{\frac{\lambda z}{2}} \tag{1.1}
\]

Current commercial photolithography systems use an ArF light source, which produces light at 193nm. Further reduction of light source wavelength has stalled in due to air absorbing wavelengths lower than 185nm, requiring the transition to an all-vacuum optical path. Industry has gone to great effort to reduce the feature resolution by implementing immersion projec-
Figure 1.1: Photolithographic method for patterning metal films. 

a) In contact photolithography, ultraviolet light selectively exposes the photoresist film. 
b) Development of the resist removes the UV exposed portions. 
c) Metal is deposited using evaporation or sputtering. 
d) Dissolution of the remaining photoresist carries away any metal not directly attached to the substrate.

1.1.1 Electron beam writing

An alternate direct write method is the use of an electron beam to expose a thin resist layer in a similar manner to photolithography. This method is capable of writing 5nm lines, and is typically what is used to form the high resolution masks used for photolithography.[11] However, due to the complexity of the system and the fact that the beam must be scanned across the entire pattern, this process is both extremely low throughput and expensive, suitable only for master pattern generation rather than large scale production. Moreover, even for experimental production of fine metal features, the process requires the use of resist films as thin as 10nm to limit spreading of the beam from backscattered electrons.[11] This ultimately constrains the
thickness of metal films which can be patterned due to the limits of lift-off.

1.1.2 Damascene process

Another method currently implemented for patterning nanoscale metal interconnects, is the damascene process, which first uses photolithography to pattern a dielectric, with metal then conformally coated to fill the cavities. Process control is required to prevent voids from being formed as the cavities are filled, but superconformal techniques have been developed to prevent this from happening.[12] However, because excess metal is deposited in undesired locations, chemical mechanical polishing (CMP) is required to planarize the substrate, a costly and difficult to maintain process.[13]

1.1.3 Nanoimprint Lithography

Physical application of a mechanical mold to replicate a pattern is known as nanoimprint lithography (NIL) and shows promise for nanoscale patterning at lower overall cost than direct write methods. Several variations on nanoimprint exist using different resist materials or transfer steps (Figure 1.2). In resist-less nanoimprint, the imprinted material can be the final metal pattern, where a hard mold applies tremendous pressure to cause plastic deformation of the metal which then takes the complementary shape of the mold.[14, 15, 16] Despite the pressure required, a residual layer prevents complete removal of metal under the deformed portions of the mold. Adding an ion milling process step has been shown to be able to remove this layer. For lower pressure processing schemes, the resist layer can be a polymer that is either heated to a molten state (thermal NIL or T-NIL), or is a UV curable liquid resin (UV-NIL ). UV curable techniques can also operate in a step and repeat process (S-FIL) that lowers the requirements on uniform pressure distribution and permits the use of small molds for patterning of entire wafers.[17, 18, 19] Mechanical imprinting with these organic resists still leaves behind a residual layer, which is often removed through reactive ion etching (RIE) to expose the underlying substrate. At this phase, metal can be evaporated onto the substrate and the liftoff procedure performed. Finally, in some cases a metalorganic resist can be used, which permits T-
NIL at lower pressured than used in resistless NIL. However it is then directly converted to metal structures by heat treatment which decomposes the resist and removes the organic components.[20, 21]

1.1.4 Electrochemical micromachining

In contrast to other metal patterning techniques, electrochemical micromachining (ECM) allows the direct removal of metal at the micro- and in some cases nano-scale. A conductive probe, acting as a counter electrode, is brought in close proximity to the metal surface (working electrode) while separated by a liquid electrolyte. When a short pulse of voltage is applied to the probe, the metal anodically dissolves in a small region around the probe.[22, 23, 24] Due to the entire substrate participating in the electrochemical reaction, the challenge in this process is to limit the etching as much as possible to the area closest to the probe. To achieve nanoscale resolution, the gap between the counter electrode and work piece is typically less than 1µm and nano-second pulses are required, allowing the etching distance around the tool to be limited to as small as 20nm. An extension of this process to increase material removal rate is to create a stamp-like pattern which when brought into proximity to a metal surface will transfer the entire pattern simultaneously, while still achieving 90nm resolution.[22]

Alternatively, rather than requiring precise control of the gap between the work piece and stamp as the feature defining property of the ECM, the EnFACE process fixes the gap size and uses a flat counter electrode, masked with an insulating layer to limit charge transfer to be across from the desired etching location on the work piece.[25] To maintain pattern fidelity, the electrochemical reactor geometry is tuned to flow the electrolyte during the etching process. However, pressure drop created by cross flow through the narrow gap limits the minimum gap size to several hundred microns, resulting in a limit in lateral resolution to approximately 120µm.

A third variant to ECM eliminates the pattern fidelity loss generated by placing the pattern-defining aspect on the tool (be it surface relief or masking) and replaces it with a mask on the substrate surface. In this case it is clear that the initial etching will occur in the desired regions due to the mask blocking electrolyte access to the surface. However, producing this
Figure 1.2: Variants of nanoimprint lithography (NIL) for patterning metal. In resistless NIL pressure is applied directly to the metal layer causing plastic deformation. In thermal NIL, the mold is heated and a thermoplastic resist flows to fill the mold. If the resist is an organometallic, heating can convert the resist to metal. In UV NIL, the liquid resist is cured using ultraviolet light through a transparent mold. For all imprinting, a thin residual layer exists that can be removed by ion milling or oxygen reactive ion etching (RIE) for organic resists. Molded thermoplastic or UV cured resists are then used in metal deposition and liftoff to achieve the final metal pattern.
mask on the substrate with nanoscale features is not trivial; it requires a patterning step similar to the e-beam or nanoimprint steps outlined above, and ultimately only allows for patterning of a single substrate. Moreover, while initial metal etching is precise, as material is removed the liquid electrolyte permits isotropic etching and undercut of the mask material. This severely limits the aspect ratio achievable.

1.2 Solid-state superionic stamping

Our group has developed an ECM process wherein the liquid electrolyte and mask required to block charge transfer with the workpiece are replaced with a single superionic solid electrolyte with nanoscale pattern embossed into the electrolyte surface. This process is given the name solid-state superionic stamping (S4) and achieves significantly greater resolution while still being able to pattern entire areas at once through the simple application of a bias voltage.[26, 27, 28, 29]

Solid-state superionic stamping, shown in Figure 1.4, utilizes a solid ionic conductor as the primary active element. The face of the stamp is fabricated to be flat, with the complement to the final desired metal features patterned...
Figure 1.4: Schematic of the solid state superionic stamping (S4) process. A stamp made of solid ionic conductor (such as Ag_2S or Cu_2S) with surface features is brought into contact with a metal film. Application of an anodic voltage between the stamp and metal film causes electrochemical etching of the metal, with metal ions flowing into the stamp. Due to being solid, the pattern on the electrolyte surface mediates the location where metal is removed. When the stamp is removed, metal remains in a complementary pattern to the features on the stamp.

in the surface. When pressed against a metal film, the electrolyte makes electrical contact with the film in all locations except where the patterned voids exist. Simple application of an anodic voltage between the stamp and metal film causes the electrochemical etching of the film at those contact interfaces, leaving the metal under the voids unchanged. Due to the application of nominal pressure to maintain contact, removal of metal results in the stamp sinking into the metal film. Unlike etching using a physical mask, the dimensions of the patterns on the solid electrolyte remain unchanged as the stamp progresses into the film, eliminating the concern of pattern erosion that occurs when a mask is undercut.

In this way, metal is removed until either the voltage is removed or the entire thickness of the film is etched, leaving only the complement to the stamp—the original desired pattern—behind. A key difference from thin film patterning using nanoimprint is the absence of a residual layer. Moreover, in contrast to direct metal imprinting, stamp pressure is only needed to establish contact, not plastically deform the metal.
1.2.1 S4 Capabilities

For S4 patterning of silver, silver sulfide (Ag$_2$S) is the most reported stamp material. This stable material is a mixed ionic conductor, with a crystalline $\beta$ phase below 177°C that is ionically conductive at room temperature.[30] In addition to silver, S4 has been extended to patterning copper using Cu$_2$S.[29] Copper sulfide, however, is a less ideal stamp material since it is only ionically conductive above 105°C. Due to the rapid oxidation of copper films at this temperature, processing must occur under an inert atmosphere which significantly complicates the process. It has been demonstrated that through the structural similarity between Ag$_2$S and Cu$_2$S, Ag$_2$S stamps can also etch copper by accommodating copper ions in low concentrations from the etched film.[28]

S4 has demonstrated remarkable resolution in the patterning of thin silver films. Figure 1.5 depicts a focused ion beam (FIB) patterned Ag$_2$S stamp and result of etching a 250nm thick Ag film with 10nm Cr adhesion layer deposited on glass.[27] In contrast to alternate resist deposition and liftoff techniques using e-beam or nanoimprint lithography, S4 easily achieves greater than unity aspect ratios limited instead by the adhesion of the silver to the substrate. The resolution is high enough, as seen in Figure 1.5c,d that even nanoscale scratches and roughness on the stamp surface are reproduced in the patterned silver.

Focused ion beam (FIB) patterning is a powerful technique initiaially used for fabricating features on S4 stamps, however it has several shortcomings. First, it is a sequential write process similar to e-beam lithography, which is inherently slow especially for writing large areas at high resolution. In addition, direct writing of a pattern on a stamp limits the pattern created to the lifetime of that single stamp which may be up to 10’s of uses.

Kumar et al. improved upon this fabrication method by taking advantage of the low hardness of Ag$_2$S for resistless nanoimprint of bulk Ag$_2$S against a silicon master mold. While the mold may be produced with FIB or e-beam lithographic techniques, the mold can be reused for as long as it is kept contamination free. Figure 1.6 depicts the <10nm gaps achievable through pattern transfer from silicon, to Ag$_2$S, and then to silver.[26]
Figure 1.5: S4 pattern transfer. a) image of focused ion beam milled Ag$_2$S stamp. b-d) Patterned 250nm thick silver film with 10nm Cr adhesion layer on glass. Letter dimensions are 200nm wide, giving better than 1:1 aspect ratio patterning. Reprinted with permission from [27]. Copyright 2017 American Chemical Society.

Figure 1.6: Bow tie pattern replicated using embossed S4 stamp. a) E-beam patterned silicon mold b) bow tie embossed into Ag$_2$S stamp c) S4 etched silver film, replicating <10nm gap between the triangles of the bow tie. [26]
1.2.2 S4 Stamp fabrication

The fundamental strength of the S4 process, stamp surface-mediated contact with a metal film, requires careful preparation of the stamp surface to approach the idealized contact depicted in schematics. Realistic concerns of stamp preparation are paramount; stamp surfaces must be both free of contaminating particles and flat, both of which are required for hard-hard contact against a flat substrate. Because of this and the high resolution pattern transfer of S4, introduction of polishing media to prepare Ag$_2$S typically yields poor results even with extremely fine abrasives since particles either remain on the surface or the scratches they produce on the stamp transfer onto the metal film during the etching step.[31] In particular the softness of Ag$_2$S leads to the embedding of particles into the stamp surface.

In practice, bulk Ag$_2$S stamp faces were prepared using an ultramicrotome and a glass or diamond blade to produce contamination free surfaces. However typical ultramicrotome machines are designed for the slicing of small, soft samples, which limit the stamp diameter to less than 1mm. Moreover, while blades typically do not introduce contamination, they often have defects and do not produce flat surfaces. Before nanoscale patterns can be applied to these surfaces, direct imprinting against a flat surface such as a silicon wafer was performed to reduce these defects.

While resistless imprinting of Ag$_2$S is useful tool for extending the usefulness of a single slow e-beam patterning step, it too suffers from the same issues as direct imprinting of metal; viz. large embossing pressure and buildup of material around features. These limit the scalability of the process as well was the types of features which can be patterned.

Given the difficulty in S4 stamp preparation, in this work an extension of S4 is made through the introduction of alternate stamp solid electrolyte: AgIAgPO$_3$ glass. Although there are several compelling reasons to use this material over Ag$_2$S, the main motivation is the material’s low glass transition temperature, $T_g$, which permits fabrication of the stamp through thermal nanoimprint, where the superionic conductor is liquid rather than solid. Initial glass surfaces can be melted to produce a near ideal, low contamination surface which when imprinted can achieve a high degree of flatness. Moreover, thermal nanoimprint overcomes the large forces required for plastic deformation and eliminates the elastic spring back which causes pile-up
around features in solid imprinting. Chapter 2 details the selection and performance of AgIAgPO$_3$ in the S4 process. Subsequently, chapter 3 updates the tooling for S4 to readily accommodate controlled thermal nanoimprint and characterizes the parameters affecting the molding process. Contamination concerns in the glass synthesis are addressed in chapter 4 along with a purification procedure.

1.3 E-beam defined silver extraction on AgIAgPO$_3$

Whereas in S4 the interface between electrode and electrolyte is dictated by texturing of the solid electrolyte surface, in the following sections the situation is reversed by controlling the electrode geometry by replacing a metal film with electron beam. Due to the poor electrical conductivity of AgIAgPO$_3$, electrons injected into the surface are confined locally and cause silver extraction in the form of nanoparticles embedded within the glass. Detailed in chapters 5 and 6, this produces colored surfaces controlled by the raster pattern of the electron beam. This phenomenon is characterized extensively for multiple beam energies and electron fluence and then harnessed to produce full color optical images with diffraction limited resolution. Chapter 5 also demonstrates that with enough charge transfer to the surface, silver can be extracted to form continuous films that follow the electron beam raster pattern. This work is extended in chapter 7 where further morphological control of the bulk silver extracted from the ionic conductor is explored. Specifically, an attempt is made to limit lateral spreading of silver extracted from the glass. In addition, the e-beam creation of embedded particles is used to define higher regions of surface electrical conductivity, allowing current applied by a simple metal probe to extract silver films in arbitrary complicated films rather than a single metal particle or fractal network.
CHAPTER 2

SOLID STATE SUPERIONIC STAMPING
WITH SILVER-IODIDE METAPHOSPHATE
GLASS

2.1 Introduction

Recently our group demonstrated an all solid-state direct patterning approach for both silver and copper films using a process called solid state superionic stamping (S4).[27, 29, 32] At the core of the process lies a patterned stamp made of a solid electrolyte (for Ag and Cu, Ag$_2$S and Cu$_2$S were pursued respectively as stamp materials) which anodically dissolves metallic films in contact with the stamp upon application of an electrical bias. As described in chapter 1, fabrication of optically flat, contamination free surface stamp comprises the largest obstacle towards nanoscale patterning. Given that these challenges described are particular to the stamp material (Ag$_2$S and Cu$_2$S), and the strong motivation of emerging applications, it is necessary to explore other ionic conductors that have the potential to improve the S4 process ability to pattern silver. In this chapter, we propose and characterize the ability of a low temperature, moldable, transparent glassy electrolyte, AgI-AgPO$_3$, for use in nanopatterning silver films.

Section 2.1 discusses different possible silver ion conductors that could be used for patterning silver and the justification for choosing AgI-AgPO$_3$ as an appropriate electrolyte for S4. Section 2.2 describes the methods for making micro- and nano-patterned stamps of this mixture and demonstrates the use of the stamps in the S4 process for high-resolution as well as large-area patterning. Section 2.3 describes the patterning results obtained and examines the electrochemical characteristics of the process.

Selecting a different superionic conducting stamp material based on desirable characteristics for the S4 process is imperative in that it can lead to better stamps and expand S4 capabilities. Specifically, by selecting a stable stamp material with a low melting point, not only does fabrication of stamps
by hot embossing/forming and nanoimprint become possible, but it also removes the need for the high forces involved in mechanical imprinting.[33, 26]

Many solid silver ion conductors are based on silver iodide (AgI), which has a low ionic conductivity below 146°C but undergoes a transition to a high conductivity α-phase above this temperature.[34] Though silver iodide itself is not a suitable room temperature stamp material, compounds made with it can have similarly high ionic conductivity while remaining conductive at room temperature.

The highest room-temperature ionic conductors are based on addition of alkali metal elements. Examples include RbAg₄I₅ and KAg₄I₅, both with conductivities of 1.2x10⁻¹ Ω⁻¹-cm⁻¹ at room temperature.[35] RbAg₄I₅ has the advantage that it can be thermally evaporated into thin films. However, RbAg₄I₅ is thermodynamically unstable below 27°C, and members of this family of conductors decompose in a matter of hours in laboratory conditions when exposed to moisture or iodine, making them unsuitable for ambient processes in a manufacturing environment.[34]

Other ionic conductors include mixtures of silver iodide with silver oxyacid salts such as Ag₇I₄PO₄, Ag₁₉I₁₅P₂O₇ and Ag₆I₄WO₄, with conductivities as high as 1.9x10⁻² Ω⁻¹-cm⁻¹, 9.0x10⁻² Ω⁻¹-cm⁻¹, and 4.7x10⁻² Ω⁻¹-cm⁻¹ respectively.[34] In particular, these types of ionic conductors are much more stable in the presence of moisture, and do not contain toxic elements such as mercury, arsenic, or cyanide.[35] In addition to their high conductivity, these materials are easier to melt-process, forming eutectic mixtures with much lower melting points than that of silver iodide alone. Mixtures of AgI and Ag₄P₂O₇ produce a eutectic point of 58°C, though this eutectic is not at the peak ionic conductivity. Mixtures of AgI and Ag₃PO₄ or Ag₆I₄WO₄ yield highly conductive eutectic mixtures with melting points of 225°C and 290°C and could have some use in the S4 process.

In contrast to the other materials mentioned, silver metaphosphate (AgPO₃) forms a stable, clear glass with a glass transition temperature of 200°C. Though the intrinsic ionic conductivity of silver metaphosphate is only 10⁻⁵, 10⁻⁷ Ω⁻¹-cm⁻¹, addition of silver iodide increases the ionic conductivity significantly at high concentrations of AgI while remaining amorphous.[36, 37, 38, 39, 40] Moreover, the linear, polymeric nature of the metaphosphate bonds is broken up with the addition of AgI, leading to a decrease in glass transition temperature with increasing AgI concentration, reaching as low as
80°C.

The very low glass transition temperature and high conductivity of $(\text{AgI})_x-(\text{AgPO}_3)_{1-x}$ make it the most promising material for use in S4. Even with the addition of silver iodide, the glass remains transparent with a gradually increasing yellow tint. The transparency of the conductive glass allows high resolution optical alignment of nanostructured features through the use of moiré patterns.[41] Unlike the mixed conduction seen in $\text{Ag}_2\text{S}$ and $\text{Cu}_2\text{S}$, metaphosphate glass remains a pure ionic conductor, simplifying the analysis of charge transfer during the etching/patterning process. This paper examines various aspects of $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ glass fabrication, its application in large stamps for the S4 process, and analysis of the etching characteristics of this material. The wide variety of glass forming and glass modifying materials available for generating silver glasses opens the possibility of future refinement of this material for the S4 process.

2.2 Materials and Methods

2.2.1 Electrolyte Preparation

Glassy $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ was prepared from AgI, AgNO$_3$, and $(\text{NH}_4)_2\text{HPO}_4$ reagents similar to well documented processes.[42, 37] Silver nitrate and diammonium hydrogen phosphate were heated to 600°C in an alumina crucible in a fume hood until the mixture finished evolving H$_2$O, NH$_3$, and NO$_2$ gasses. Then the material was heated to 700°C for 3 hours, before being quenched between aluminum plates. The resulting glass shown in figure 2.1a was crushed, mixed with AgI, and again heated to 700°C for 16 hours in a covered alumina crucible before being quenched again. The final glass is transparent yellow with embedded small white particles. X-ray diffraction confirmed that the resulting material is primarily amorphous with some samples showing small silver iodide peaks. Figure 2.1 shows $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ glass mixtures prepared with $x=0.25$, 0.35 and 0.45, with the $x=0.45$ sample having the lowest glass transition temperature and highest conductivity as measured by electroimpedence spectroscopy. Subsequent stamps were made using an $x=0.50$ formulation of the glass for the slightly lower glass transition temperature and higher conductivity.
2.2.2 Forming the Electrolyte into Small Stamps

The process for making AgI-AgPO$_3$ stamps with diameters ranging from 300-1000 $\mu$m is shown in figure 2.2. First, the glass is crushed into a powder and deposited in a blunt stainless steel needle. The needle is then heated above the glass transition temperature to make a glass plug. With minimal air pressure this plug is moved to the tip where it creates a hemispherical protrusion. Subsequent cooling of the glass maintains this shape. The next step is to heat a silicon master mold to greater than 80$^\circ$C, above the glass temperature of the stamp material. The needle is then brought down onto the surface, melting and flattening the glass, imprinting nanoscale features on the surface. Finally, the substrate is cooled at a rate of 1$^\circ$C/min to 70$^\circ$C before being demolded by lifting the stamp and separating it from the mold.

2.2.3 Forming Large-Area Stamps

Large-area stamps, with diameters of several millimeters, were made by nanoimprinting. These stamps were formed using PDMS replica molds of
Figure 2.2: Small S4 stamp-making process. a) AgIAgPO$_3$ glass fills a needle and is heated until the glass forms a hemispherical tip. b) The unfinished stamp is pressed against a heated master mold and cooled slowly below the glass transition temperature. The stamp is then removed from the mold leaving an impression on the glass. c) Pressing the stamp against a silver film and applying 100-400 mV etches the stamp pattern into the film.
a silicon master pattern. The silicon pattern was coated with a nonstick coating of tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (FOTS) using vapor deposition. Next, a 10:1 ratio of PDMS was cast over the silicon master. Upon removing the silicon pattern the PDMS mold was also treated with FOTS. The AgI-AgPO$_3$ stamp material was then molded in the PDMS mold at 175°C for 25 minutes in an oven. A small weight was applied on the glass to promote full surface contact with the PDMS mold.

2.2.4 Substrate Preparation

Silver films for metal patterning were prepared on clean silicon wafers or glass cover slides that were first cleaned with a fresh 5:1:1 solution of deionized water, hydrogen peroxide, and ammonium hydroxide at 70°C for 10 minutes. Silver was then deposited 30-300 nm thick by electron beam evaporation (Temescal e-beam evaporator) using a thin layer of Ti or Cr for adhesion.

2.2.5 S4 Patterning of Silver Films

For patterning of silver, the stamp must be in physical contact with the silver film. Due to the limited control our setup allowed on cooling of the stamp after hot embossing, the thermal contraction of the glass imparted a mild curvature to the stamp surface. To compensate for this curvature, a moderately high pressure of 50-120 MPa was used to make conformal contact between the stamp and silver film. Wedge misalignment was compensated by observing the quality of the first few etches, followed by manual tip-tilt alignment. Contacts were made by connecting the needle to the counter electrode and the silver film to the working electrode of a Gamry Reference 600 potentiostat working in chronoamperometry mode with voltage biases set at values ranging from 90mV to 400mV. Completion of etching was identified by a sharp drop in the measured electrical current. To ensure completion of the patterning, the voltage bias was maintained for an additional few seconds.
Figure 2.3: Silicon pattern and etched silver patterns on silicon. a) Silicon mold used for nano-imprinting. b,c) Scanning electron micrographs showing S4 patterned silver with feature widths down to 160 nm. Scale bar is 1 micron. d-f) AFM and SEM images of complex geometries etched with glassy S4 process.

2.3 Results and Discussion

2.3.1 Small Stamp Mold Patterns

Two stamps were fabricated based on the procedure outlined in the previous section for small stamps. For the first stamp, the pattern that was hot-embossed into the stamp is shown in figure 2.3a. This pattern was made using conventional microfabrication processes. The height of the relief structure was 67 nm for use with 40 nm silver films patterned in these experiments. Small area stamps were imprinted with the silicon pattern containing 100 nm to 500 nm features, with an overall area measured to be 0.26 mm² using SEM images of the etched silver films. Hot embossed stamps retained the high resolution patterns of the mold, though recessed features were occasionally difficult for the glass to wet, and sometimes air was trapped at the glass-mold interface. Thin anodized aluminum with 105 nm pitch pores was grown for use as a shadow mask for the second mold.[43] Electron beam evaporation was used to deposit 25 nm of nickel through the mask onto a silicon wafer. Removal of the alumina template results in a mold of hexagonally arranged 60-80 nm dots seen in figure 2.4.
2.3.2 Silver Pattern Quality

Figure 2.3b-e shows several images of a silver pattern after S4 etching with the first imprinted stamp, including complex patterns and sub-160 nm wide lines. Lines wider than 300 nm were reliably formed without difficulty. Line spacing of 100 nm was achieved with this pattern, however incomplete wetting of the stamp to the master mold caused lower yields on long, closely spaced lines that are spaced less than 200nm apart and some isolated etching areas. Figure 2.4 shows the silver pattern resulting from the stamp imprinted with the anodized aluminum templated mold. The silver dot diameters range from 40-70nm with the separation between particles is as small as 30nm.
2.3.3 Process Efficiency

Since this electrolyte is a pure ionic conductor, the total charge and mass transported across the interface are expected to be nearly identical once steady etching is established. For the nanoimprinted small stamp, integration of the current profile for each chronoamperometry curve yields the total charge for each run and shows that the stamp quickly reaches a constant value of $105 \pm 1 \, \mu C$ as seen in figure 2.5. This value is independent of the voltage used to etch the silver. Calculated from the area and thickness of the stamped region, the total charge due to removed silver is $99 \pm 5 \, \mu C$, demonstrating that the chronoamperometry data provides an accurate indication of the etching progression. In contrast, materials like Cu$_2$S have a significant electronic current component in addition to the ionic current.[29] Moreover, since the stamp is a pure ionic conductor, the silver ions from the anodic dissolution on the substrate-stamp interface do not recombine with electrons near the stamping interface during etching, instead depositing out on the back side of the stamp on the cathode.

The average etch rate was determined by dividing the film thickness by the time required to reach 10% of the maximum current density. Due to the quick drop in current around this time, it represents the end of the etch process. Figure 2.5c plots these etch rates versus voltage and a linear relationship can be seen. A minimum voltage of 90 mV is needed to initiate etching above which the etch rate linearly increases. For voltages above 300 mV the etch rate exceeds 20 nm/s which greater than five times the etch rate achieved with Ag$_2$S stamps. A detailed analysis of the etch rates also reveals that for a given voltage the etch rate increases slowly with repeated use of the stamp. This may be due to silver dendrites seen forming of on the cathode, increasing the electric field gradient for each subsequent run.

2.3.4 Large Area Patterning

In addition to the parallel nature of S4 pattern transfer, large area stamps were also prepared in a parallel manner using thermal nano-imprinting. This process allowed fabrication of stamps of several square millimeters as quickly as small stamps given a master pattern. In this work, two master patterns consisting of grating patterns with 3 µm pitch and 500 nm height (Micro-
Figure 2.5: S4 process characterization. a) Typical chronoamperometry curves of 40nm silver film with etch rates of 11.5 nm/s and 2.6 nm/s for applied voltages of 250 mV (solid) and 125 mV (dashed) respectively. b) Charge transferred by one stamp in a sequence of several etches. All etching runs above the cutoff voltage result in nearly the same charge. c) Relationship of applied voltage to etch rate with rates varying from 0.5 nm/s to 26 nm/s.
Figure 2.6: Large area patterns etched in silver over a 2-5 mm diameter. 
a,b) silver grating created with $3\mu m$ pitch over 2 mm diameter. c,d) 
periodic holes etched over 5 mm diameter area.

Masch TGZ03) and a PDMS replica mold of silicon pillars of 15 $\mu m$ diameter 
and 30 $\mu m$ height were used. With uniform applied pressure, both patterns 
were reproduced in silver films over 6 mm$^2$ and 25 mm$^2$ areas respectively. 
Figure 2.6 shows the results of large area patterning using the S4 process 
with AgI-AgPO$_3$ stamps.

2.4 Conclusions

Silver iodide silver metaphosphate glasses provide a significant improvement 
over the previously reported superionic stamping with crystalline stamp ma-
terials. We have demonstrated etched silver features as small as 30 nm re-
produced from a nickel mold by S4 with a glass stamp with nanoscale dots. 
Micron-sized patterns were molded on several millimeter wide stamps which 
were successfully transferred onto silver films, demonstrating the capability 
of large area patterning.

The purely ionic conduction and lack of grain boundaries in this glassy
conductor make it a promising material to study for the direct metal patterning. The low glass transition temperature makes melt-processing feasible and allows S4 to benefit from advances in thermal nano-imprinting. Finally, the silver metaphosphate glass system is very rich with materials that can be added to further refine glass transition temperature, ionic conductivity, and durability of stamp material. Overall, our approach provides an economical and practical pathway for industrial-scale implementation of solid state superionic stamping.

2.5 Acknowledgments

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CHAPTER 3
MACHINE DESIGN,
CHARACTERIZATION, AND PROCESS
IMPROVEMENT FOR SOLID-STATE
SUPERIONIC STAMPING

3.1 Introduction

Chapter 2 outlined a major advance in solid-state superionic stamping (S4) through the introduction of AgI AgPO₃ glass with favorable material properties. It demonstrated the proof of concept that an ionically conductive glass could be used as a stamp with thermal nanoimprint being used to fabricate the nanoscale patterns on the stamp. Moreover, it characterized the high resolution and etch rates possible when using a material with high ionic conductivity and near unity silver ion transference number.

However, the approach taken in the previous chapter can be improved upon in several ways. The needle-based glass forming technique is useful for millimeter sized stamps, but scales poorly for stamps larger than 1-2 mm. The long dimensions of a needle make tip/tilt alignment difficult and cannot support moderate loads. Moreover, the brittleness of the glass requires that there be a firm attachment of the glass to the stamp holder to prevent the glass from breaking in undesired locations during demolding. As stamps are designed for larger dimensions, stamp fracture due to differences in coefficient of thermal expansion also become more prominent.

In addition to difficulty in demolding of stamps, thermal nanoimprint at larger scales will induce larger stresses due to volumetric thermal contraction from the glass transition temperature, $T_g$, to the S4 processing temperature (typically at 20-25°C). This contraction plays a significant role in determining the overall flatness of the stamp after molding. Since the S4 process involves nanoscale deviations in solid-solid contact, even a subtle variation of a few hundred nanometers across the stamp surface are sufficient to prevent silver etching in large portions of the stamp. Most surface deviations are on millimeter or larger length scales compared to the micro or nanoscale silver
patterns, allowing some flattening to take place during etching by the application of downward pressure to the overall stamp. It is still highly important to maintain stamp flatness during the molding procedure, however, since the overall load needed by the system increases with total stamp area.

This chapter is focused on improving the system upon which S4 is conducted, its characterization, and further process improvement. Using AgIAgPO$_3$ as the active component in S4, a hybrid stamp is developed to facilitate stamp manufacture, alignment, and use. Moreover, the peripheral hardware for the S4 process is greatly improved to increase controllability and repeatability of the process. Using this upgraded machine, the molding process can be characterized in greater detail. Furthermore, the standardization of stamp manufacture can allow a transition to process advancement of S4 and integration with other processes.

3.1.1 Introduction of a New S4 Machine

The goal of upgrading the equipment for the S4 process is twofold: to accommodate glass stamp areas up to 10mm in diameter as well as to improve the overall process control. Figure 3.1 shows the platform developed for S4 is based on a 4-axis system (XYZΘ) with substrate-side XY brushless linear stages (Aerotech#ALS20020) along with a linear z-stage (Aerotech #PRO165-05MM) with linear brushless theta stage (Aerotech #ALAR150-LP). Tip /tilt alignment can be performed manually to account for variations parallelism. The substrate side platen consists of a temperature controlled surface to which spring clips can be used to secure molds and substrates as well as attach the substrate-side electrode for S4. To the theta-axis are mounted two 75lb load cells (Transducer Techniques #MLP-75) to which the temperature controlled stamp holder is attached. The system is capable of supporting 17.5kg (38lbs) limited by the x-axis. The stamp holder secures in place the S4 stamp for both molding—through thermal nanoimprint—and the S4 process, and allows electrical connectivity to the stamp.
Figure 3.1: Overall view of the S4 machine, with axes and important components labeled.
3.1.2 Hybrid S4 stamp

Although AgIAgPO\textsubscript{3} is the active component of an S4 stamp, integration of the brittle glass into the S4 process benefits from the creation of a hybrid stamp, shown in Figure 3.2, that includes additional materials and features to facilitate the process. To make secure mechanical and electrical connections to the S4 machine, the glass is melted into a metal ring. Based on the high thermal expansion coefficient of AgI\textsubscript{2}(AgPO\textsubscript{3})\textsubscript{1-x} glasses—26.8 ppm/°C for AgPO\textsubscript{3}—the ring material was chosen to be aluminum, which has a similar thermal expansion coefficient of 23 ppm/°C.[44, 45] This limits the chance of thermal stress induced fracturing during the temperature cycling of the molding process. Moreover, 100nm of silver was sputtered onto the aluminum to prevent the formation of any aluminum compounds at the interface and to provide a similar electrochemistry with silver films to be etched in S4. To allow through-stamp visibility, provide scratch resistant surface, and provide mechanical support for the active glass, a BK7 glass window is inserted behind the silver glass. Though the window could be adhered in place permanently, it was found that the silver glass flowing into the clearance between the window and the aluminum was sufficient to fix the position of the window. This is true as long as the aluminum ring of the stamp remains below the T\textsubscript{g} of the silver glass, which is the case in the molding process explored for S4 at the moment.

Mounting an S4 stamp encompasses several practical challenges to address the different functions the stamp is to perform. Figure 3.3 gives a cross section view of the stamp and associated stamp holder. Since imaging through the stamp is limited by the working distance of the optical microscope, the overall stamp and stamp holder thickness is limited to 30mm. Due to the moderate compressive load supported by the stamp holder, most of the vertical space is occupied by the stamp holder, which has a large cutout to prevent obscuring the optical path of the microscope. This necessitates a low profile, compact clamping method for the stamp, which also is expected to experience moderate load in compression and light loads in tension. To overcome this challenge, a quasi-kinematic solution was developed. A point-contact based kinematic design is not suitable for supporting large compressive forces. Instead, the base of the stamp is supported by the flat surface of the stamp holder, with position accuracy controlled through elastic averaging.
Figure 3.2: Hybrid S4 stamp. The silver coated aluminum ring allows easy handling of the stamp and provides a strong connection to the AgIAgPO$_3$ glass. The 30° chamfer allows quasi-kinematic locating of the stamp, while the flat bottom gives sufficient contact area to support large loads. The marked cylindrical portion is machined to 12.7 mm which allows scale calibration for images taken from the side.

However, the stamp must also withstand low loads in tension that exceed what can be achieved with vacuum support. The quasi-kinematic portion of the stamp comes from 3-line contact (often reduced to 3-point contact due to manufacturing errors) established between the lower portion of the stamp and the stamp holder. The stamp features a conical chamfer on the stamp that mates with two inclined planes on the stamp holder shown in Figure 3.4a. Figures 3.4b,c show that with the addition of a second set of inclined planes that form a dovetail, inserting and capturing of the stamp by the stamp holder can be accomplished with minimal dexterity. The third contact point, also on an incline, is inserted into the dovetail and secures the stamp into position with tightening of a screw.

3.1.3 Heaters: Design

To apply heat to the stamp and to the mold, resistive wire heaters were implemented separately on the stamp holder and mold/substrate stage. Although it is common to operate resistive heaters on relay-switched mains voltage, the large amount of electromagnetic noise generated by both the
Figure 3.3: Cross Section of the S4 tool: the stamp holder and stamp. The fixturing mechanism for the stamp must be thin to allow the stamp surface to be within the working distance of the optical microscope.

Figure 3.4: Clamping system for S4 stamps. a) the stamp mates against the upper surface and points along two inclined planes in the back. b) a dovetail slot accepts the stamp from the side. C) the stamp slides into place and d) a clamp inserts into the dove tail and provides pressure holding the stamp against the rear contact points. The angled contact surface also provide upward clamping pressure to eliminate any clearance between the stamp and the upper surface.
high-voltage AC as well as the switching itself is not tolerable for the sensitive electrical measurements used for S4. Moreover, relay-switched heaters tend to oscillate around their set point based on the switching frequency. Due to the large change in properties of AgIAgPO$_3$ near the $T_g$, lower noise variable DC power supplies were used instead. Adjustable DC power supplies were made by modifying 75V 400W switched mode power supplies so that the output voltage could be controlled by external analog signal.

To prevent excessive heating of the load cells supporting the stamp holder, Teflon spacers were used to minimize heat flow into the sensors. Despite this effort moderate heating of the load cell results in thermal drift of up to 0.8lbs of the load reading with variations in stamp holder temperature from 20-100°C. The substrate heater is also supported by Teflon minimize heat flow into the XY stages. Both heaters have K-type thermocouple feedback into thermocouple amplifiers which send analog voltage to the control system.

3.1.4 Heaters: Temperature control

Figure 3.5 diagrams the control loop used to achieve precise temperature control of both the stamp holder and the mold/substrate hot plate. The control system is designed to be linear in response to heat generated, taking the square root of the output to send the desired voltage signals. The primary control algorithm is a feed-forward control effort based on one dimensional heat flow. To maintain a given temperature in steady state, the resistive heat generated (equation 3.1) by the heaters must equal the heat lost to the environment (equation 3.2). Equation 3.3 demonstrates that fundamentally the steady state voltage, $V_{ss}$, needed at the heater is proportional to the square root of the difference of the setpoint temperature, $T_{sp}$, above the ambient temperature $T_a$. Simple steady state calibration of the heaters sufficient to determine the feed-forward gain, $k_{ff}$, needed.

$$Q = \frac{V^2}{R}$$  \hspace{1cm} (3.1)

$$Q \propto h(T_{sp} - T_a)$$  \hspace{1cm} (3.2)

$$V_{ss} \propto \sqrt{(T_{sp} - T_a)}$$  \hspace{1cm} (3.3)
Figure 3.5: Temperature Control Loop. The power applied to the resistive heater is the sum of a feed-forward power used to estimate the power required for maintaining an elevated temperature, $T_{sp}$, above ambient, $T_a$, in steady state, plus a PI feedback loop to reduce rise time and any remaining steady state error between the measured temperature, $T_m$, and $T_{sp}$.

While the feed-forward path takes care of the steady state power required, a feed-back loop is used to obtain a faster response time and to eliminate steady state errors caused by non-ideality. The loop implemented is proportional-integral in design, with saturation on the integral value. The closed loop gains, $k_P$ and $k_I$, were tuned to give a stable response with fast rise time and small overshoot. Figure 3.6a demonstrates a step response from 40°C to 60°C of the substrate heater. The red portion of the curve is where heating is limited by the maximum voltage of the power supply. In the yellow section the control loop is approaching the set point, while in the green portion the set point temperature has been reached. Due to the thermal inertia of the systems it was determined that derivative control in the feedback loop was not necessary. As can be seen in Figure 3.6b, there is only 0.16°C overshoot and the system is capable of stabilizing the temperature to significantly better than 0.1°C. Thermocouple temperature measurements were made using AD8495 precision thermocouple amplifiers, which have a temperature accuracy of 1°C.

Most of the temperature control used for S4 is to maintain constant temperature during each step, with the exception of cooling of the stamp after molding. To maintain a constant ramp rate while cooling, a simple traveling $T_{sp}$ was established at the desired cooling rate. This was found effective for passive cooling at rates of 1°C/min or less for temperatures above 60°C.
Figure 3.6: a) Step input for heater increasing from 40°C to 60°C. In the red region, maximum power is being generated by the heater. In the yellow region, the feedback contribution to heater power is being decreased until the set point is reached at the green region. b) Plot of temperature overshoot and resulting temperature stability.
3.1.5 Load Control

In addition to the implementation of precise temperature controls, load control on the stamp is an important feature of the new S4 system. A simple practical reason makes clear why this is necessary. During the cooling process after molding, several cooling parts contract as the temperature decreases. Since the stamp is rigidly attached at the stamp holder, the stage must move to maintain contact with the mold until the appropriate demolding temperature. Implementation of constant load feedback during the cooling process solves this issue.

Moreover, controlled load makes both the molding and S4 processes much more repeatable. During molding, consistent load will affect the glass flow rates and make it possible to calibrate molding times. In the S4 process application of load can be used to mitigate small flatness errors or to avoid stamp fracture from excessive forces.

A discrete controller for velocity was implemented for a force feedback system (Figure 3.7). This controller consists of a proportional gain, along with velocity saturation and a dead band. Velocity saturation was included as a safety feature to prevent high velocity commands from being sent to the stages. Due to the finite time interval between control loops iterations, this avoids stage crashes. Though not strictly necessary, a small dead band of ±0.04lbs was implemented in the controller to avoid excessive direction switching when operating within the noise error of the load cells. This avoids unnecessary load on the stages. Finally, the proportional gain, $k$, was tuned to put the force feedback system near critically damped to give a fast response without load overshoot.

![Figure 3.7](image_url)

Figure 3.7: Discrete velocity controller. a) Diagram of velocity magnitude sent to stage depending on force error. Control scheme is proportional, with both a dead band for low errors and a maximum velocity $v_{max}$ for large errors. b) Diagram of load and velocity of the stamp.
Figure 3.8: Approach, contact and load control. a) Total load applied to the stamp as it makes contact with the substrate. In the period from $0 < t < 2$ the load increases due to the motion of the stage and the stiffness of the overall system. b) System maintaining load for constant (I), increasing (II), and decreasing (III) stage temperature.

Figure 3.8 demonstrates the typical load performance for molding or application of S4. In the for $t < 0$, the stamp is not in contact but approaching the surface. For most commanded loads, this results in the stage travelling at $v_{max}$ until contact is made. At $t=0$, the elasticity of the system is evident and the load increases at a maximum rate as the stage continues at $v_{max}$, until approaching the set load value. Then the stage slows and comes to rest within the dead band of the set load. Figure 3.8b shows several cases on maintaining a prescribed load of 10 lbf. In section I, the stage is maintained at 60°C, requiring little height adjustment. At the beginning of section II, the temperature is ramped, increasing the pressure in turn. Here the stage makes minute adjustments to keep the load within the dead band. A similar case can be seen in section III, where the heaters are turned off and the $z$-axis must accommodate for the thermal contractions in the system.
3.1.6 Through-stamp imaging

The optical microscope on the S4 machine was already part of the system when built and includes a high magnification zoom lens column. The illumination incorporated into the system is dark field, accomplished by a ring light attached to the front objective. Figure 3.9 highlights the light path in different illumination schemes of dark field, transmission, and coaxial illumination. While dark field illumination is useful at highlighting abrupt surface changes formed on S4 stamps, it was found that the large angle of incidence of the illumination resulted in very little light reaching the stamp surface. Moreover, since only a portion of the scattered light is collected by the microscope, the collection efficiency in dark field is very low requiring long exposure times. Due to inadequate illumination, the primary focus was to demonstrate the feasibility of imaging through an S4 stamp.

Figure 3.10a,b demonstrates optical imaging on the S4 system using a transparent mask with backside illumination. From this system one can see rectangles on a 100µm pitch viewed through the stamp. It is clear that quality imaging requires glass that is free of bubbles and particles. However, in locations free of these inclusions, the edge contrast indicates resolution of features at least as small as 9µm is achievable. The imaging performance with backside illumination is promising, however many nanoscale molds are made of silicon and most substrates to be etched are coated with a continuous layer of silver which make them opaque.

In future versions of S4, the optical system would benefit from coaxial
Figure 3.10: Optical images taken through S4 stamps. a,b) Image taken of transparency using backside illumination. Scale bars are 1 mm and 100 µm respectively. c) Image of silver squares on silicon taken on a different optical system using coaxial illumination. Scale bar is 1 mm.

illumination as shown in Figure 3.9c, where a beamsplitter introduces illumination along the same optical path used for imaging. While the current S4 system lacks this capability, a similar camera system with coaxial illumination on another system includes it. Figure 3.10c demonstrates imaging of silver squares on a 100 µm pitch on silicon and demonstrates similar performance despite the light used for illumination passing through though the stamp twice.

In addition to the change in lighting strategy, there are several factors that affect imaging quality. Of highest importance is the reduction of inclusions within the glass, and this will be addressed in chapter 4. Imaging quality is also affected by the refractive index of AgIAgPO₃, which has a large dispersion and varies with composition (see Figure 6.2). The high index of refraction of AgIAgPO₃ also acts to shorten the working distance of the microscope. Future iterations of stamps may replace the optical window with a diverging lens to lessen this effect.
3.2 Experimental characterization of AgIAgPO$_3$ imprinting

The development of low $T_g$ glass stamps for S4 is directed towards simplifying and standardizing the stamp manufacturing technique to increase the yield of the S4 process. Chapter 2 described implementation of high resolution S4 stamps with diameters less than 1mm using thermal imprinting on rigid molds. Nanoimprint for larger stamps onto rigid molds was limited due to handling challenges during the demolding process. While generation and use S4 stamps were successfully demonstrated over distances of up to 5mm, their fabrication required the use of flexible and low surface adhesion polydimethylsiloxane (PDMS) replica molds. These silicone molds are not ideal due to the difficulty in replicating nanoscale features accurately. Moreover, reliably generating flat stamps with polymer molds is challenging due to the high thermal expansion coefficient and low thermal conductivity of polymers combining to distort the mold when thermal gradients are present. In this section, a process for molding S4 stamps against rigid master patterns is characterized, based on the procedure first created for small stamps in Chapter 2.

3.2.1 Stamp preparation

Initially, the components of the hybrid stamp as assembled on a heated glass slide at 180°C, well above the glass transition temperature AgIAgPO$_3$. At such high temperatures, AgIAgPO$_3$ can wet the metal ring and optical widow, and though capillary action fill the space between the two. The flatness of the glass slide will ensure that the optical widow remains in the correct position until the AgIAgPO$_3$ has solidified. AgIAgPO$_3$ is added to the cavity with care taken not to introduce bubbles which would obscure the clarity of the glass. Enough glass is added as to fill the cavity and also generate a 2-3mm protrusion, as tall as the surface tension of the glass will allow. This generates a rounded surface with a single tallest point. The glass is then allowed to cool to room temperature. If the AgIAgPO$_3$ surface becomes contaminated, the top portion can be removed, replaced with clean glass, and re-melted to reform the convex curvature. For previously used S4 stamps, as long as excessive silver plating of the glass has
not occurred, stamps can also be regenerated by simple heating.

3.2.2 Molding process description

![Diagram of molding process](image)

Figure 3.11: Plot of sample AgIAgPO$_3$ imprinting process. A heated hybrid stamp containing a convex AgIAgPO$_3$ surface is brought into contact at $T = 0$ with a mold heated above the glass transition temperature $T_g$ of AgIAgPO$_3$. Constant load is applied as the stamp contact with the mold increases in the red highlighted portion. In the yellow highlighted region the load is reduced to a nominal value to maintain contact with the mold, yet let flow induced stresses dissipate. In the cyan region, the temperature of the mold is decreased to below $T_g$. Finally in the green region tension is applied to separate the glass stamp from the mold.

After clamping into the stamp holder on the S4 machine, the initial step in the molding process is to bring both the stamp and mold to temperatures of $T_s$ and $T_m$ respectively. For molding to occur, $T_m$ must be above the glass transition temperature of AgIAgPO$_3$ (80-105°C, depending on glass processing), while $T_s$ should remain below $T_g$ to prevent dislodging of the glass window. Figure 3.11 depicts the mold and stamp holder temperatures along with the load applied to the stamp. First, highlighted red in Figure 3.11, the stamp is brought into contact with the mold under constant load.
Due to the fixed overall thermal gradient between the stamp holder and the mold, only a region adjacent to the mold flows significantly. The thickness of this layer depends upon the location of the isothermal line corresponding to a temperature of \( T_g \), or the temperature several degrees above \( T_g \) where viscosity is sufficiently low that flow can be observed at a practical timescale. Initially, load is concentrated on the small contact area, resulting in large stresses which spread the glass contact area quickly before decreasing in speed.

When the desired stamp diameter is reached, the load is lowered to a small value, \( F_a \), for a short time (typically 1lbf for 1min) to allow the viscoelastic flow stresses to relax. \( F_a \) must remain compressive to avoid lifting of the mold. The cyan section on Figure 3.11 depicts how the mold is then allowed to cool such that \( T_m < T_g \) and the stamp has completely solidified. Separation of the mold from the stamp is then accomplished by removing the compressive load on the stamp and, if necessary, applying tension until brittle fracture of the mold-stamp interface occurs.

The main challenges for molding S4 stamps with diameters of several millimeters are producing flat surfaces and cleanly demolding the stamps at the end of the procedure. Due to many factors such as viscoelasticity of the glass, thermal contraction during solidification and cooling, and load induced elastic deformation of the mold, the resulting stamp surface can experience significant curvature which inhibits the contact needed for S4. This section attempts to characterize several process parameters and how they relate to stamp curvature. Moreover, successful demolding requires the fracture of the mold-stamp interface rather than fracture within the glass which both ruins the stamp and contaminates the mold. To reduce the adhesion to the mold a well-known 'non-stick' silane coating is applied to the mold to verify whether the coating can withstand the temperature and potential chemical attack of molten glass.

### 3.2.3 Stamp curvature dependence on mold material and mold temperature \( T_m \)

At the nanoscale, typical rigid materials for molds are either silicon or oxides such as SiO\(_2\). To investigate whether there is a preferred mold material,
4mm diameter stamps were molded against a silicon wafer (500µm thick) and an optical flat (6.15mm thick) under a load of 10lbf. Profilometry was performed as the primary metric of flatness for the stamps. Though both materials are hard, they differ by two orders of magnitude in terms of thermal conductivity with values of 148 W/m·K and 1.38W/m·K for silicon and fused silica respectively. Thus while silicon molds can be assumed to be in equilibrium with the hot plate temperature, fused silica molds require calibration to achieve the desired surface temperature of the mold.

![Image](image_url)

Figure 3.12: Surface profile of stamps molded against a silicon wafer and a fused silica optical flat for several temperatures. Note that the face of the stamp is aligned upwards for profilometry, such that the above curves represent concave surfaces.

Figure 3.12 shows the average surface profile of stamps with $T_g$=100-105°C molded using 10lbf against both a silicon and fused silica at surface temperatures ranging from 110°C to 120°C with the stamp holder heating naturally to approximately 40°C. The stamp surface in both cases is concave. Between the materials, the silicon wafer performed better than the fused silica, despite the better initial flatness of the optical element. It is hypothesized that the thick silica layer does not maintain as uniform of a temperature as with silicon. Coupled with the difficulty in calibrating the surface temperature of a thermal insulator, continued characterization was
limited to the use of silicon molds. Due to the large change in viscosity with temperature, the molding time at 110°C (5-10°C above $T_g$) lasted for 1-3 hours, while molding at 120°C required less than 10 minutes. However, there is no clear trend in concavity with the mold temperature despite the large difference in molding time. This allows the mold temperature, $T_m$, to be chosen to imprint such that the imprint time is 1-5 minutes, slow enough to control the final stamp size, but fast enough such that the imprinting itself becomes a minor portion of the total time fabricating an S4 stamp.

3.2.4 Stamp curvature dependence on imprinting load $F_m$

Figure 3.13: Profilometry of several S4 stamps imprinted against silicon under loads of a) 10lbf and b) 30lbf. For each plot, the average of the scans is plotted in black.

When operating at temperatures approaching $T_g$ as just shown, the flow
rate of the glass is determined by the pressure applied rather than dominated by other forces such as surface tension or gravity. As such, the imprinting time can be reduced by applying a larger load to the stamp. Figure 3.13 demonstrates the resulting curvature of several stamps molded to 4mm in diameter under loads of 10lbf as well as 30lbf. For clarity, the averages of the scans are displayed in bold. Under 10lbf load, Figure 3.13a shows that stamps on average have approximately 500nm total surface deviation, with variability in the result of approximately ±100nm. Under 30lbf load, stamps tended to have 600nm total surface deviation with variability of ±200nm. It is possible that the larger forces may produce more concave surfaces with less reliability because they induce larger viscoelastic strain within the stamp, such that the one minute relaxation period is insufficient for built up stresses to be removed before stamp cooling. Alternatively, it is possible that the localized loading by the stamp causes bending of the mold. This will is explored later through finite element modeling.

3.2.5 Stamp curvature dependence on stamp holder temperature $T_s$

While the mold temperature is primarily determined by the stamp glass transition temperature, $T_g$, and the desired imprinting time, the temperature of the stamp holder can also be varied, effectively tuning the thermal gradient within the stamp. Initial molding experiments were carried out without temperature control of the stamp holder, however the stamp holder reached steady state temperatures of nearly 40°C due to heat transfer from the heated mold surface. Implementation temperature feedback in the stamp holder allowed better control of the process. In Figure 3.14a, stamps ($T_g=81^\circ$C) were molded to 4.5mm diameter against silicon maintained at 98°C with the stamp holder fixed at temperatures ranging from 38-80°C. As is evident by the color progression, in cases where the stamp holder was at 60°C or below, the stamp surface was concave. However at higher temperatures the concavity reversed, producing convex stamps. To summarize the results of these scans, each surface profile was fit by a quadratic function. Figure 3.14b extracts just the quadratic coefficient and plots it as a function of stamp holder temperature. Clearly, the stamp holder temperature directly
and significantly affects the curvature of stamps made through imprinting, despite no similar effect being seen for the mold-side temperature.

Compared to molding with a lower stamp holder temperature resulting in central 500-600nm gaps when performing S4, heated stamp molding offers the ability to lower the gap to <100nm or even reverse the concavity slightly to allow contact to first occur in the center of the stamp. Due to the remaining variability in surface curvature, reliably achieving less than ±100nm from a nominal gap size remains challenging. It is hoped that with further refinement of the molding process, this variability can be reduced even further, permitting lower forces in the subsequent S4 etching.

3.2.6 Effect of cooling rate and stamp size

A final examination of the molding process parameters concerning overall stamp flatness suggests that the cooling rate of stamps after imprinting may affect the resulting stamp curvature. Thermal contraction during the cooling process is a source of internal stresses which can deform the stamp, however these stresses are relaxed if to a degree if the viscosity is low enough. Figure 3.15 examines additional stamps (Tg 85°C) formed similar to those in Figure 3.14, but varies the cooling rate of the mold after imprinting between 0.5°C/min and 1.5°C/min. However, there appears to be little difference in the resulting curvature. Thermal simulations of the system place the thermal equilibration time at less than 5min, meaning that throughout the 12-36min cooling period the system remains near thermal equilibrium and thus any variations would be due to viscous relaxation of thermal stresses. A cooling rate of 1.5°C/min is the maximum achievable with passive cooling on this system, however lowering the mold temperature at higher rates with active cooling may result in significant stamp changes.

3.2.7 Parameters affecting the imprinting time

In addition to examining the flatness of stamp surfaces, the time involved in the imprint itself was examined more thoroughly as a function of mold temperature and the desired stamp diameter with results shown in Figure 3.16. Since the main restriction to an increase in stamp diameter is the flow rate
of the glass, the change in viscosity of the glass with temperature is the dom-
inant parameter when varying mold temperature. In the temperature region
immediately above Tg, viscosity follows the Vogel-Tamman-Fulcher (VTF)
model with viscosity exponentially with $T^{-1}$. Thus it is not surprising that
molding times also vary exponentially with mold temperature. Interestingly,
this same behavior is seen when the molding time is measured as a function
of stamp radius. Due to the creation of an approximately uniform liquid
layer in contact with the mold, the process follows Darcys law, in a well-
known expression for one dimensional radial flow, which predicts logarithmic
growth in the stamp diameter, or exponential growth in imprinting times as
a function of diameter.

The characterization in Figure 3.16 is ultimately useful because it provides
a simple method for predicting molding times. Given that the mold temper-
ature is known not to significantly affect stamp curvature, when attempting
to form a stamp of an increased or decreased size, the molding temperature
can be adjusted to maintain nearly constant imprinting time. This avoids
poor size control when imprinting small stamps as well as keeping imprinting
times reasonable in transition to fabrication of larger stamps.

3.2.8 Reducing demolding forces using a fluorinated coating

Adhesion of the stamp to the mold is another challenge of using molten
glass in imprinting. After the mold has cooled to 70°C, the silicon molds
are removed by brittle fracture. While it is often the case that the stamp
cleanly delaminates from the mold, the brittleness of silicon imparts risk of
mold destruction when doing so. Much more likely is that small portions of
the stamp glass around the perimeter of the contact area remain adhered to
the mold after delamination. This mold contamination can be removed but
requires extended soaking in aqua regia. Progression of stamp manufacture
to larger areas naturally is expected to result in larger forces required for
demolding, and therefore reducing the adhesion strength between the stamp
and mold is of high importance.

Many in the nanoimprint community are aware of this problem and often
imprint materials are chosen with low surface energy to facilitate demolding.[46]
In the case of S4 however, simple replacement of the stamp material is not
possible since many of the properties of the glass—including low $T_g$, ionic conductivity, and chemical durability—are required for molding and S4 etching. Chemical modification of the ionically conductive glass to lower the adhesion to mold materials may be possible in future studies, but will require extensive research to identify alternatives.

An alternate method for reducing mold adhesion is to coat the mold surface with a low surface energy material. Fluorinated trichlorosilanes provide a convenient route to low adhesion surfaces since they can be deposited via chemical vapor deposition and form a strong covalent bond with hydroxyl terminated surfaces. They are commonly used as mold release agents silicon and silicon dioxide surfaces, where minimal nonstick coating thickness is desired.

The adhesion reducing properties of tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane (FOTS) were explored for use in imprinting with AgIAgPO$_3$ glass against silicon. Treated silicon wafers were first RCA cleaned (5:1:1 of water : ammonium hydroxide : hydrogen peroxide for 10 minutes at 60-70°C) and then treated to 100W O$_2$ plasma for 1 minute to create a clean hydroxyl-terminated surface. The silicon was then placed in a vacuum jar with a few drops of FOTS and left under vacuum for 1hr. Samples were then rinsed in toluene to remove any excess adsorbed silane.

S4 stamps were then imprinted with 10 lbf against silicon at 98°C with the stamp holder at 60°C to form 4.5mm diameter stamps before the load was reduced to 1lbf and the mold was cooled at 1°C/min. Figure 3.17a shows the loading results of demolding at 70°C by raising the stage at 1µm/s. When stamps were separated from bare silicon, mold adhered to the stamp, resulting in tensile loading. While the magnitude maximum tensile load varies between stamps, it was found to be significant at up to 3 lbf. Figure 3.17b shows an identical set of experiments using the silane treated silicon. For these samples there is no overall tension. Instead, the slight curvature of the stamp induces localized tension near the center of the stamp and compression near the periphery. As the contact-maintaining load diminishes, the central tension is sufficient to cause delamination of the mold, as evidenced by the abrupt loading changes. While stamps demolded from bare silicon often leave small debris around the periphery of the stamp, in none of the experiments with silane coated silicon was this observed. Thus in addition to a higher likelihood of successful delamination, the anti-adhesion coating
preserves molds to last for many more imprinting cycles.
Figure 3.14: a) Profilometry scans of S4 stamps imprinted against silicon for different stamp holder temperatures. b) Coefficient of quadratic component fit to the line scans. The crossover from positive to negative values indicates a switch from concave to convex surfaces depending on the stamp holder temperature.
Figure 3.15: Quadratic component of the surface fit versus stamp molding temperature for 4.5mm stamps fabricated with slow cooling of 0.5°C/min (circles), fast cooling of 1.5°C/min (diamonds), and larger 6.5mm stamps. No varying the stamp cooling rate or diameter causes no significant change in curvature between these processing conditions.
Figure 3.16: Surface and contour plot of the molding time required to reach a given stamp diameter using the prescribed mold temperature. Molding time appears exponential in both independent variables, resulting in a plane when plotted on a logarithmic scale. Color map and contour levels are plotted at exponentially increasing intervals.
Figure 3.17: Force measured in separating stamps molded against a) bare silicon and b) FOTS coated silicon.
3.3 Modeling

The previous experimental analysis showed that the flatness overall of surfaces generated by thermal imprinting depends upon the temperatures and loading used. To gain some additional insight into the factors that can affect flatness and ultimately contact during the S4 process, some simple models are explored here. While temperature dependent viscosity and thermal contraction likely account for a significant portion in the surface curvature, examining a fully time-dependent, fluid dynamic simulation is outside the scope of this work. In this analysis, attention will be paid to the steady state thermal gradients, the potential bending of the mold under load, and the force required for fully achieve contact in S4, given a non-flat stamp.

3.3.1 Modeling thermal gradients in the molding process

Due to the exponential change in viscosity of AgIAgPO$_3$ at temperatures near the glass transition temperature, the thermal gradient within the glass of the stamp directly affects the flow profile during imprinting, as well as the degree to which those viscoelastic flow stresses as well as thermal strains can relax within the time period of the imprinting process. To model the thermal gradients within the glass during the molding process, a 3D axisymmetric model of steady state heat transfer was developed in COMSOL Multiphysics software.

The model, shown in Figure 3.18, incorporates the connections between the stamp and stamp holder, as well as a mock mold made of silicon and supported on an aluminum base. Stamp holder is made of aluminum. As with most of the experimental data, the contact diameter of the stamp with the mold is 4.5mm, while the glass filled cavity is 6.5mm in diameter and the distance between the stamp ring and the mold is 2mm. At the boundary of the simulation, both the aluminum supporting the mold and the aluminum of the stamp holder are maintained at a constant temperature of 98°C and 40°C respectively. Heat transfer is prohibited along the central axis due to axial symmetry, while the upper air boundary convectively cools the system convective to an ambient temperature of 20°C with a heat transfer coefficient of 10W/m$^2$·K).

Due to the arrangement of the materials, there are two thermally conduc-
Figure 3.18: Axisymmetric thermal model of the stamp molding process. The boundaries of aluminum stamp holder are held at 40°C, while the lower boundary of the aluminum supporting the silicon mold is held at 98°C.

tive assemblies that experience very low thermal gradients, separated by a thermally insulating AgIAgPO$_3$, glass, and air layer. The thermal conductivity, density, and heat capacity, $C_p$, of AgIAgPO$_3$ was taken to be 0.259 W/m·K, 5.38g/mL, and 305 J/(kg·K).[47]

Figure 3.19 shows the thermal gradient developed in the system at steady state. Isothermal lines have been included along with a black isothermal line at 90°C—10°C above $T_g$—to indicate an approximate boundary between solid and molten glass. The low thermal conductivity of AgIAgPO$_3$ allows a portion of the heat to travel up the central axis, within the glass portion surrounded by aluminum. Interestingly, the silica glass window, with a higher thermal conductivity of 1.38 W/m·K serves to spread the heat slightly and bring the rear portion of the stamp to a more uniform temperature. Closer
Figure 3.19: Thermal simulation of steady state temperature of stamp during molding. White lines are isothermal lines, with the black line at 90°C indicating roughly the transition between solid and liquid within the AgIAgPO$_3$.

to the mold surface, the glass experiences much larger thermal gradients. To first approximation, there is a uniform molten layer, which matches the observation that the glass flow rate is similar to that found in 1D radial flow. However, the slightly warmer center combines with the curved feature along the perimeter of the contact between AgIAgPO$_3$ and silicon, to result in a tapering of the molten layer thickness towards the perimeter of the stamp.

Solidification of the glass and creation of internal stresses upon cooling depends upon many factors, but is likely dominated by the uniformity and thickness of this liquid layer. A more uniform liquid layer could be developed by maintaining a constant cross section of AgIAgPO$_3$ from mold to the stamp ring, along with establishing the thermal uniformity of the back of the stamp. When cooling, the interplay between relaxation of molten glass and the inherent thermal stresses generated by cooling through the glass transition with a significant thermal gradient are likely to be a primary cause of
curvature in the final stamps. However due to the complexity of a coupled heat transfer and viscoelastic fluid flow simulation, this analysis is left for future work.

3.3.2 Modeling mold deformation during imprinting

Despite lacking a full fluid dynamics model to predict stamp overall stamp curvature, there are still several aspects of the molding process that can be analyzed to determine their likely contribution to overall curvature. One aspect that can be analyzed simply is the glass-silicon interface deformation due to the pressure applied during molding. In a typical molding process, the stamp is kept under light pressure during cooling in order to maintain thermal contact with the mold. As seen in Figure 3.20, for a 10N load this effect is negligible, reaching just over 3nm deviation between the center and edge of the stamp.

![Figure 3.20: Relative elastic deformation of the mold due to stamp loading of 10N.](image)

Another circumstance which could affect the curvature of the mold—and therefore the resulting stamp—during molding is if the silicon mold is poorly supported beneath the stamp. Figure 3.21 depicts this arrangement which causes plate bending; the load applied by the stamp is transferred laterally to
a simply supported portion of the mold outside the diameter of the stamp. Figure 3.22 details the result of simulations of a 10N applied force as a function of the radius from the central axis of the stamp to a simply supported location on the silicon mold. Of main concern is the relative height change from the central axis to the edge of the stamp, which can be seen to quickly rise to above 100nm for an unsupported radius of 4mm, then slowly increase with increased radius. However the underlying assumption of this model, namely that there is a small gap under the mold allowing bending, is only valid so far as the gap can be considered to still be present after deflection of the silicon. With increased span between supports, the total vertical travel increases sharply. Thus, placing an upper limit of 10µm in the assumed initial gap height results in a maximum amount of stamp height variation of 200nm if the stamp were unsupported for a radius of 8mm.

![Figure 3.21: 2D axisymmetric mold bending model caused by the mold being simply supported on high points of the mold heater outside the area of stamp contact.](image)

Overall, this analysis provides an upper bound to the curvature in the mold experienced during the molding process and the likelihood of such poor support of the mold is low. However, as can be seen by the sharp increase in stamp height variation for even small spans, the flatness of the mold support
can lead to variations in the range of 100nm, or a significant fraction of the flatness found in molded stamps. Thus it is important that the support for silicon molds be both flat and free of surface contamination could lead to these support conditions.

![Graph showing variations in stamp surface height and total mold displacement under a 10N load as a function of support span.](image)

Figure 3.22: Variations in stamp surface height and total mold displacement under a 10N load as a function of support span.

3.3.3 Modeling elastic compensation for stamp curvature

Although empirical investigation of the molding process revealed ways to lower the stamp curvature through proper temperature choices, often a parabolic concave or convex curvature remains. However, this curvature may result in a total of only ±300nm of deviation from the center to the edge of the stamp. Experimentally it was found that to at least some extent, simply compressing the stamp is sufficient to make contact across the entire stamp surface. To understand the expected magnitude of the load required to compensate for this stamp curvature, a contact simulation was developed for stamps with parabolic curvature resulting in an initial no-load gap of 125nm to 2µm.

Figure 3.23 depicts the simulation domain, consisting of a 2D axisymmetric model in ABAQUS with an upper AgIAgPO₃ glass domain contacting a lower
silicon domain which is attached to a rigid foundation. The nominal contact
diameter is 4mm, however initially the contact area is very small due to the
stamp curvature. When load supplied through traction along the side of the
glass domain is increased, the gap closes until there is hard contact across
the full diameter of the stamp. The load required to achieve full contact
was then measured for various initial gap sized. Both concave and convex
surfaces were modeled, resulting in positive and negative initial gap sizes
respectively.

Figure 3.24 shows an apparent linear relationship between the initial gap
size and the load required to generate full contact. Of particular interest is
the asymmetry between concave and convex surface and their respective load
requirements. Though ideally one would generate completely flat stamps, the
statistical variation seen in the molding requires consideration of whether
convex or concave stamps are preferred. Comparing concave and convex
surface with the similar gap sizes, concave surfaces require 3.37 times the
load to make full contact. This suggests that generating convex surfaces
are preferable to concave ones. Additionally, for concave stamps the load
is maximum along the periphery of the stamp. This can be an issue when
performing S4 on softer surfaces such as plastic, since the high load may
cause excessive strain in the substrate at the edge of the stamp and result in
tears along the silver film. Finally during the demolding process, separation
of the stamp from the mold requires brittle fracture of the interface. In order
for cracks to initiate, they must be under tension. The generation of slightly
convex stamps can facilitate this by initially placing the periphery under
tension upon the release of molding pressure. Together these effects suggest
that better overall performance will achieved by designing for a slight bias
towards convex stamps.

3.4 Improvement to S4 process

As shown in previous chapters, performing S4 etching requires the application
of a potential between the metal film to be etched and the stamp. In
many cases, the silver deposition step is performed by simple evaporation or
sputtering, causing the entire substrate to be coated—and therefore electrically conductive. This allows easy application of a probe to a substrate, as
long as the substrate is larger than the stamp. However, in many processes, it is preferable to use photolithography and lift-off to pattern silver from millimeter domains down to the microscale level on the substrate, leaving isolated domains of silver behind. Although S4 is capable of removing these large features, it makes mold fabrication more difficult.

S4 patterning on isolated domains of silver is possible as long as there is sufficient electrical conductivity between these domains and the location of the probe. For example, patterning on highly doped silicon poses no issue. However, for patterning on isolated silver domains on a low-doped silicon substrate, one cannot rely on the conductivity of the underlying substrate.

To achieve electrical conductivity to these domains, an additional continuous metallic layer can be deposited prior to the deposition and initial patterning of silver using photolithography and lift-off. Both chromium and titanium are common adhesion promotion layers typically used for silver and were explored additional use as this conductive layer. While both metals are effective at adding electrical conductivity, their presence electrically connecting all silver domains is most likely unwanted after S4 patterning. Thus titanium was chosen as since it can be etched in hydrofluoric acid, which does not attack silver or the underlying silicon substrate.

Figure 3.25 depicts application of this technique where 10nm of titanium was evaporated on a blank silicon wafer. Next, standard photolithography, metal evaporation and lift-off was performed to deposit 9µm patches of 200nm silver. To produce nanoscale gratings, an S4 stamp was molded against a 606nm period silicon grating, then used to etch the silver island substrate.

3.5 Conclusion

Overall the tooling for performing S4 has been greatly improved. Implementation of a hybrid stamp that meets both the electrochemical needs of S4 along with practical handling concerns makes stamp fabrication a routine task. Through implementation of precision temperature control in the stamp molding process, the stamp produced is both of higher quality and made with better repeatability than in previous generations of the process. Future work for S4 continues in an effort to generate increased area contact.
One route is through the continued exploration of factors that affect stamp flatness, with more accurately flat stamps facilitating hard-hard contact. Another option to explore is the application of S4 on softer polymer substrates such as polyethylene terephthalate (PET) and cyclic olefin copolymers, where slight macroscale imperfections in stamp flatness can be accommodated by elastic deformation of the substrate, while transferring the desired nanoscale features.

In addition, continued work is needed to understand factors that affect stamp lifetime and reliability. Although AgIAgPO$_3$ is more resistant than many silver ion conductors to environmental factors, it is known that over time the surface of the glass is degraded by water moisture. Through chemical modification of the glass it may be possible to significantly increase the resistance to water while still retaining the beneficial properties that make AgIAgPO$_3$ favorable for use in S4. Finally, continued refinements are needed to make S4 integrate well in the typical multistep microfabrication process.
Figure 3.23: Finite element contact model. Initial stamp surface contains a small parabolic curvature preventing contact except at a single point. Load is applied via traction on the side of the stamp, gradually closing this gap and creating hard contact between AgIAgPO$_3$ and a silver coated silicon substrate used in S4. Note: the size of the gap (125nm - 2µm) makes visualizing the gap difficult.
Figure 3.24: Load needed to make full contact between stamp and substrate in S4, depending on the gap generated by a parabolic stamp surface. Concave stamps initially have a center gap that is positive, while convex stamp make contact at the center with the gap at the outer edge of the stamp (negative initial central gap distance).
Figure 3.25: Example of isolated 9μm silver domains S4 patterned with a 606nm period grating. A thin layer of titanium deposited prior to photolithography and silver deposition provides surface conductivity from the isolated domains to an electrical probe located several millimeters away. After S4 patterning, the titanium can be removed with a quick dip in hydrofluoric acid.
CHAPTER 4

AGIAGPO$_3$ GLASS SYNTHESIS: AN ANALYSIS OF CONTAMINATION INTRODUCED THROUGH LOW COST CRUCIBLES

4.1 Introduction

AgIAgPO$_3$ is an inorganic glass that possesses an unusually low glass transition temperature, $T_g$, along with ionic conductivity on par with liquid electrolytes. Recently it has been incorporated into several processes that rely on high transparency of the glass. Solid state superionic stamping uses nanopatterned surfaces where the transparency of the ionic conductor can aid in process alignment. Moreover, silver nanostructures can be extracted on the surface through electron beam interaction. The transparent nature of the substrate allows interrogation of these structures in transmission, given the optical properties of the glass can be well characterized. [48, 49, 50, 51, 52, 53, 54, 55, 56]

Properties of (AgI)$_x$(AgPO$_3$)$_{1-x}$ glass are known to depend upon the synthesis method. Musterelli et al. noted that simple exposure of the precursor compounds to laboratory air containing moisture was sufficient to cause large variation in glass transition temperature. Due to water hydrolyzing the phosphate chains and inserting stable -OH$^-$ end groups, it is difficult to drive off requiring heat treatment for several hours at 700°C.[57] The susceptibility of the glass to this attack also dictates the solubility of phosphate glasses, with some phosphates such as NaPO$_3$ being readily dissolved in water while others with divalent or trivalent metal ions such as Fe(PO$_3$)$_3$ are more water resistant than window glass.[58, 59] The glass former AgPO$_3$ lies between these extremes, containing a monovalent cation but remaining relatively stable in the presence of water.

More recently, Konidakis et al have noted an additional factor that plays a significant role in the final glass: the crucible material. [60] The preferred crucible material for most glass synthesis is an alloy of Pt/Au, chosen both for
inertness at high temperature as well as its non-wetting nature. However, the large expense of platinum crucibles results in much research being conducted in less expensive alternatives. Two common crucible materials are high purity alumina and quartz.[40, 61, 38] In many publications, the crucible material used is not mentioned.

While alumina crucibles are suitable for most high temperature synthesis, they are prone to attack by hot phosphoric acid and its anhydrous form P₂O₅. However, the suitability for various metal metaphosphates is less clear. Water soluble sodium metaphosphate melts are known to significantly attack alumina crucibles, producing visible etching of the crucible sidewall.[62] Much less soluble Ca(PO₃)₂ and Mg(PO₃)₂ glasses also display bulk alumina contamination ranging from 3-7% Al₂O₃ when melted in an alumina crucible, though the attack of the crucible is less severe. Since AgPO₃ is less prone to hydrolysis than NaPO₃, the level of alumina contamination is expected to be less, though still measurable. Konidakis et al. have shown that upon synthesis of AgPO₃ and (AgI)ₓ(AgPO₃)₁₋ₓ, the corrosive nature of the phosphate etches the crucible, incorporating Al₂O₃ into the glass melt.[60] Use of P₂O₅ as a phosphate precursor at 700°C was found to lead to approximately 3% alumina contamination. However, when synthesized using the less corrosive (NH₄)H₂PO₄ at an even higher temperature of 900°C, a lower level of contamination was evident, although this work did not attempt to determine the quantity of alumina found in the less contaminated glass. Given the low melting points of all reactants, such high temperatures may not be needed for synthesis, potentially allowing for less contamination by lowering the temperature of synthesis and associated chemical attack of the crucible.

Synthesis of AgIAgPO₃ in other affordable crucibles such as quartz or pyrex may also pose some difficulty. Silver possesses low solubility in silica glasses, instead often reducing to form silver nanoparticles that impart the well-known yellow color to the glass.[63] Though the phosphate environment surrounding the silver in AgPO₃ is more oxidizing than silica, the exposure to silica contamination at high temperatures is likely to have a reducing effect on the silver.

In this work, the effect of affordable crucible use for the synthesis of AgIAgPO₃ is explored. Several compositions of (AgI)ₓ(AgPO₃)₁₋ₓ glass are synthesized in alumina crucibles, with an effort to understand and minimize the effect alumina crucibles have on producing optically transparent glass. A
simple purification of these glasses is demonstrated, as well as the results of alternative preparation in commonly available quartz and nickel crucibles.

4.2 Materials

$\text{AgI}_x(\text{AgPO}_3)_{1-x}$ was synthesized from the appropriate molar amounts of AgI (99.9% from Alfa Aesar) and amorphous AgPO$_3$. AgPO$_3$ was fabricated in the lab from AgNO$_3$ (99.995% from Salt Lake Metals) and (NH$_4$)H$_2$PO$_4$ (>98% from Sigma Aldrich) in an alumina crucible on a hotplate at 550°C. Due to the significant amount of gas given off during this process, the temperature is slowly ramped up to prevent bubbling over of the melt. The AgPO$_3$ melt was then quickly quenched onto aluminum plates to preserve the amorphous structure.

Alumina crucibles (99.6%) were obtained from AdValue Technology. Nickel and quartz crucible purities were 99.6% Ni and 99.998% SiO$_2$ respectively. Phosphate glass soaking was performed in Pyrex 9800 glass culture tubes.

4.3 Experimental

$\text{AgI}_x(\text{AgPO}_3)_{1-x}$ is synthesized in three different low cost crucibles: alumina, quartz and nickel. Glass made in alumina and nickel crucibles also undergo a fining process to remove particles. The resulting glasses are then characterized to identify contamination elements.

4.3.1 Alumina crucible processing

Since phosphate glasses tend to begin evaporating P$_2$O$_5$ at high temperatures, loss of the phosphate portion of the glass is possible if the melt remains at high temperature for significant periods. Moreover, since the crucible is the suspected source of particulate contamination, limiting the glass exposure to Al$_2$O$_3$ is preferred. As such, when combining AgI and AgPO$_3$ in alumina crucibles, the kiln temperature was kept at 600°C for only 1hr for the initial fusion—above the 558°C melting point of AgI—before being ramped down to 400°C over the course of 2 hours. During the initial fusion, particles are
observed forming on the crucible walls and floating to the glass surface. Figure 4.1 shows a sample of the particles. Identification and removal of these particles is the main goal of further processing.

![Particles found within glass. Scale bar is 100 µm.](image)

As a first step in refining the glass for the removal of particles, the glass was transferred to Pyrex culture tubes when the kiln reached 400°C. With the production of particles occurring along the crucible walls, the glass was carefully decanted from the crucible using pre-heated glass burettes. At this point, the culture tubes were left undisturbed for 60 hours before cooling slowly to room temperature. The addition of AgI to AgPO₃ glasses results in very stable glasses, for which quenching to maintain the amorphous structure is usually not necessary.

4.3.2 Quartz and Nickel crucible processing

As a common alternative to alumina crucibles, quartz and nickel crucibles were also used to synthesize AgIAgPO₃ from AgI and AgPO₃. For each crucible in this method, the reactants were melted at 600°C for 1 hour. Glass from the quartz crucible was then quenched onto an aluminum plate. Nickel crucibles have a maximum operating temperature of 600°C in air, so after the initial fusion the crucible temperature was lowered to 400°C and left to soak for 24 hours before slowing cooling in the crucible. Of the crucibles materials tried, nickel is expected to be the most resistant to phosphate corrosion, though it is potentially susceptible to exchange with silver in a
single-displacement reaction. Table 4.1 compile the list of glasses A1-A7 and their associated processing parameters.

Table 4.1: Processing parameters for the synthesis of \((\text{AgI})_x(\text{AgPO}_3)_{1-x}\).

| \(\text{AgI} \) % | \(\text{Crucible material} \) | Firing temp. | Firing time | Soak vessel | Soak temp. | Soak time | Column height |
|------------------|-------------------------------|--------------|-------------|-------------|------------|-----------|
| A1               | 0 Al\(_2\)O\(_3\)           | 550°C        | -           | -           | -          | -         |-           |
| A2               | 12.5 Al\(_2\)O\(_3\)        | 600°C        | 1 hr        | Pyrex       | 400°C      | 60 hrs    | 39 mm     |
| A3               | 25 Al\(_2\)O\(_3\)          | 600°C        | 1 hr        | Pyrex       | 400°C      | 60 hrs    | 47 mm     |
| A4               | 37.5 Al\(_2\)O\(_3\)        | 600°C        | 1 hr        | Pyrex       | 400°C      | 60 hrs    | 49 mm     |
| A5               | 50 Al\(_2\)O\(_3\)          | 600°C        | 1 hr        | Pyrex       | 400°C      | 60 hrs    | 52 mm     |
| A6               | 50 SiO\(_2\)                | 600°C        | 1 hr        | -           | -          | -         |-           |
| A7               | 50 Ni                        | 600°C        | 1 hr        | Ni          | 400°C      | 24 hrs    | 12 mm     |

4.3.3 Glass characterization

The optical transparency of glass samples were determined by melting the samples into 3 mm thick disks against glass slides to produce optically clear windows. The transparency of the samples were measured on a Cary 5000 spectrophotometer in transmission mode. Energy dispersive X-ray spectroscopy (EDS) was conducted on a JEOL 6060LV SEM to determine the composition of the glasses, as well as that of the particulates. X-ray diffraction (XRD) of the glass containing a high concentration of particulates was conducted on a Philip X’pert MRD using the Cu K\(_\alpha\) wavelength.

4.4 Results and Discussion

Results of silver glass synthesis in several crucible materials. Electron imaging, elemental mapping, diffraction analysis, and optical imaging results are presented.
4.4.1 Synthesis with Al₂O₃ crucibles

Particle Identification

Whereas the work of Konidakis noted the presence of aluminum contamination in glass fired in alumina crucibles, Figure 4.1 shows that there are also crystalline particles that form within the glass.[60] While alumina content within the glass matrix affects the glass transition temperature, the inclusion of particles strongly scatter light passing through the material. The optical clarity of these glasses is of high importance in optical fiber applications as well as for imaging through stamps used in the S4 processes. [48, 49, 50, 51, 52, 53, 54, 55, 56]

Figure 4.2: a) SEM Image of contaminant particles found within AgIAgPO₃ glass synthesized in Al₂O₃ crucibles. b) Secondary electron image and elemental map of the major elements in glass and particles. Particles appear to have a high concentration of aluminum, phosphorus, and oxygen, while being free of silver and iodide.

To identify the composition of the particles, a sample from A5 was taken which contained a high concentration of particles. Figure 4.2a shows an electron micrograph of these impurities. The nonconductive nature of the particles, compared to the ionically conductive glass matrix, is clear by the charging on the particles caused by the electron beam. Figure 4.2b shows a speedmap highlighting the relative elemental composition of the particles when compared to the bulk glass matrix. As expected, the glass matrix demonstrates significant silver, iodine, phosphorous and oxygen, with a low aluminum signal. However, the particles appear free of silver and iodine,
instead being primarily composed of aluminum, phosphorous and oxygen. Quantitative EDS reveals that the ratio of P:Al in the particles is 3.06, which is consistent with a compound containing trivalent aluminum and monovalent metaphosphate. Using X-ray diffraction, this particle containing sample can be conclusively identified as containing Al(PO₃)₃ within the typical glass matrix.

![XRD spectrum of concentrated particles within AgIAgPO₃. The diffraction lines for Al(PO₃)₃ are plotted as well, which match up with the crystalline peaks seen in the glass.](image)

Figure 4.3: XRD spectrum of concentrated particles within AgIAgPO₃. The diffraction lines for Al(PO₃)₃ are plotted as well, which match up with the crystalline peaks seen in the glass.

Glass Fining

With the identity of the contaminant known, an attempt can be made at separating the particles from the bulk of the glass. The glass fining process considers the terminal velocity of bubbles within a melt to determine the effectiveness of buoyancy at removing bubbles from the bulk. While this theory is typically used for bubble removal, it also applies to sufficiently light particles. For a spherical particle acted upon by buoyancy forces, the upward terminal velocity, $v$, is given by

$$v = \frac{2gr^2(\rho_p - \rho_m)}{9\eta}$$

(4.1)

where $r$ is the particle radius, $\eta$ is the glass viscosity, $g$ is the acceleration due to gravity, and $\rho_p$ and $\rho_m$ are the densities of the particle and glass.
melt respectively. In this case $\rho_p$ is $2.71 \text{g/cm}^3$ for Al(PO$_3$)$_3$. Due to the high concentration of silver and iodide in $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ glasses, this family of glasses have exceptionally high density when compared to silicate glass. The density of AgPO$_3$ is $4.48 \text{g/cm}^3$, while AgIAgPO$_3$ has an even higher density of $5.43 \text{g/cm}^3$.\cite{38} This high density suggests that a significant buoyancy force is present on the contaminant particles.

For particle separation to work effectively, not only does the difference in density between the particles and the glass need to be large, but the viscosity of the fluid should be lowered as much as possible. Kobayashi, Takahashi, and Hiki have shown that the viscosity of both AgPO$_3$ and AgIAgPO$_3$ follow the Vogel-Fulcher-Tammann (VTF) relation similar to other simple linear polymers such as polystyrene.\cite{64} For sample A5, which is expected to be the most easily refined due to low $T_g$ and high density, equation 4.1 is rearranged in equation 4.2 to solve for the minimum particle size that travels the length of the column, $h$, during the soaking period, $T$. After an initial 24 hours soaking, it is predicted that all particles greater than $3.81 \mu m$ should be removed, and by the full 60 hour soak period, all particles greater than $2.45 \mu m$ should be absent.

$$r = \sqrt[9]{\frac{9h\eta}{2gT(\rho_p - \rho_m)}}$$

(4.2)

As is evident in figure 4.1, the majority of particles are approximately 9-10 $\mu m$, correctly predicting that sample A5 would be mostly cleared of particles as shown by 24 hours. Figure 4.4 shows that after a 60 hour soak period, samples A4 and A5 are clear to the eye. However, the higher viscosity of A3 results in only partial clarification. A2 was the least successful due to the noticeably higher viscosity which in only half of the column visibly clarified. Moreover, the low AgI content allowed small AgPO$_3$ crystals to form in sample A2.

Figure 4.5 shows the transmission of the glasses A1-A5. Silver metaphosphate, A1, is transparent throughout the visible and well into the infrared region. Addition of silver iodide creates a strong absorption below 410nm due to the resonance of free ionic silver. Due to scattering from the crystals in A2, there is significantly less transmission throughout the spectrum. However, glasses A3-A5 are quite clear with increasing silver iodide content causing the absorption cutoff to shift further into the visible spectrum.
Eliminating prolonged exposure to alumina crucibles prevents continued generation of Al(PO$_3$)$_3$ particles, but the long soaking times at 400°C in Pyrex potentially lead to ion exchange with the molten glass. Because of this, EDS was carried out on samples A1-A5, with a focus on both the major components as well as detected trace elements.

The ratios of the main constituents of A1-A5 indicate that the overall composition of the glass remain close to the nominal values. Aluminum is
detected in all glasses in the range of 0.5-0.9%, which is consistent with 
$\text{(NH}_4\text{)}\text{H}_2\text{PO}_4$ less aggressively attacking the crucible than $\text{P}_2\text{O}_5$. Since glass A1, the $\text{AgPO}_3$ used as a reactant in mixing all other glasses, contains a similar amount of aluminum to the other glasses, it is likely that a large portion of the aluminum incorporated into the matrix takes place during the initial synthesis of formation of $\text{AgPO}_3$. Subsequent mixing with AgI continues to add aluminum to the glass, but primarily leads to the formation of $\text{Al(PO}_3\text{)}_3$ crystals.

While several additional trace elements are detected, the source of several of them remain unclear. Silicon is detected in all samples in the range of 1.4-2%. While attack of Pyrex during the soaking period could account for the presence of silicon, glass A1 also includes 1.5% Si, despite not coming in contact Pyrex. Likewise, very low levels of sodium and magnesium are detected despite the crucible and initial reactants containing less than 0.1% of each.

Table 4.2: EDS analysis of the elemental composition of $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ synthesized in alumina crucibles.

<table>
<thead>
<tr>
<th>Main Constituents</th>
<th>Trace Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>I</td>
</tr>
<tr>
<td>A1</td>
<td>32.0%</td>
</tr>
<tr>
<td>A2</td>
<td>35.9%</td>
</tr>
<tr>
<td>A3</td>
<td>36.0%</td>
</tr>
<tr>
<td>A4</td>
<td>38.4%</td>
</tr>
<tr>
<td>A5</td>
<td>39.8%</td>
</tr>
</tbody>
</table>

4.4.2 Synthesis with Quartz and Nickel Crucibles

Synthesis of AgIAgPO$_3$ in alternative crucibles of quartz and nickel crucibles attempts to avoid the introduction of additional aluminum contamination while fusing AgI and AgPO$_3$. Figure 4.6 shows a comparison of optical images of the typical particle size found when using the different crucibles. For reference, Figure 4.6a shows $\sim$10$\mu$m $\text{Al(PO}_3\text{)}_3$ cubes found to be the primary scattering source in glasses fused in alumina crucibles. The fining process described above allows these large crystals to rise to the surface, while remaining less effective for particles $<6\mu$m as seen in an image from A5 shown in Figure 4.6b.
Sample A6 was prepared in a quartz crucible without an additional fining step. Figure 4.6c shows that without additional exposure to Al₂O₃, the glass remains free of large particles. However, the interaction between the crucible and the melt is significant, inducing coloration to the glass that renders it somewhat green in reflection and red in transmission. This is consistent with nanoscale silver precipitation seen in other glasses. [65]

Sample A7 was synthesized in a nickel crucible and included a fining step similar to samples A2-A5, but remained in the nickel crucible for this lengthy step. Despite this, Figure 4.6d shows that the glass is free of particles greater than 1µm and remains free of the tint found in sample A6. Figure 4.7 shows a comparison of the transparency found for AgIAgPO₃ when synthesized in the 3 different crucibles. Sample A6, melted in a quartz crucible, displays
strong absorption throughout the majority of the visible region despite being free of large particles. Sample A5, fired in alumina and refined, is much more transparent above the cutoff wavelength, but still contains particles below 6µm in size. Since the majority of the scattering was due to particles 9-10µm in size, this glass remains significantly more clear than if left unrefined. However, it is glass A7 that retains the benefit of both techniques: no additional large particle generation or tinting due to nanoscale silver particle formation.

![Graph showing optical transmission of AgIAgPO₃ glasses A5, A6, and A7.](image)

Figure 4.7: Optical transmission of AgIAgPO₃ glasses A5, A6, and A7, which were prepared in alumina, quartz, and nickel crucibles respectively.

Optically, the effect of quartz and nickel crucibles have been demonstrated on the synthesis of AgIAgPO₃. However, as with the use of alumina crucibles, it is prudent to examine whether the crucible material is being incorporated into the bulk glass. Table 4.3 shows EDS analysis of samples A5-A7. It can be seen that even a relatively short exposure to silica of A6 compared with the lengthy fining process undergone by A5 has resulted in a doubling of the Si detected. The increased silicon content is the likely reason for the formation of silver nanoparticles and resulting coloration of the glass. Similarly, a trace amount of nickel was detected in sample S7, though the extent of the impact this has on the glass needs further study. Addition of other multivalent metal ions is known to increase the connectivity of the phosphate matrix, leading to both increased glass transition temperatures and chemical resistance.[66, 67]
Table 4.3: EDS comparison of AgIAgPO$_3$ made in different crucibles.

<table>
<thead>
<tr>
<th></th>
<th>Ag</th>
<th>I</th>
<th>P</th>
<th>O</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A5</strong></td>
<td>39.8%</td>
<td>20.2%</td>
<td>19.6%</td>
<td>16.8%</td>
<td>0.4%</td>
<td>1.2%</td>
<td>0.7%</td>
<td>1.4%</td>
<td>x</td>
</tr>
<tr>
<td><strong>A6</strong></td>
<td>39.0%</td>
<td>20.3%</td>
<td>19.7%</td>
<td>14.8%</td>
<td>0.7%</td>
<td>1.4%</td>
<td>1.4%</td>
<td>2.8%</td>
<td>x</td>
</tr>
<tr>
<td><strong>A7</strong></td>
<td>40.1%</td>
<td>19.1%</td>
<td>22.4%</td>
<td>15.9%</td>
<td>x</td>
<td>1.4%</td>
<td>0.6%</td>
<td>x</td>
<td>0.4%</td>
</tr>
</tbody>
</table>

4.5 Conclusion

It is clear that the quality of (AgI)$_x$(AgPO$_3$)$_{1-x}$ glass depends significantly upon the fabrication method. Exposure to moisture before or during synthesis drastically reduces the glass transition temperature through water incorporation into the phosphate structure. Likewise, the corrosive nature of phosphate melts act severely on many crucibles. While the most inert crucible is a Pt alloy, many researchers do not adhere to its use due to the high cost involved. Substitution with alumina crucibles leads to alumina incorporation along with formation of Al(PO$_3$)$_3$ crystals. The majority of these crystals can be separated by gravity through extended soak periods in a non-contaminating container such as Pyrex. Another alternative crucible material, quartz, was found to survive the glass fusion, but cause significant silicon contamination which leads to silver reducing and rendering the glass opaque. Finally, nickel crucibles were found to be a viable alternative that did not reduce the clarity of the glass. For applications where glass of high transparency with few inclusions is required, this appears to be an adequate choice. Further study is needed to determine the effect of nickel incorporation on the glass transition temperature, ionic conductivity, and chemical durability of silver phosphate glasses.
5.1 Introduction

Silver nanoparticles display strong coupling in the visible spectrum due to the metal’s high conductivity and bulk plasmon frequency in the ultraviolet.\footnote{68} Glasses containing silver have long been produced with the plasmonic resonance of silver nanoparticles imparting a yellow tint.\footnote{69} Silver plates, octahedra, cubes, and stars can all be made in solution synthesis techniques such that they absorb light throughout the visible spectrum.\footnote{70, 71, 72} This bottom up approach shows remarkable control over the particle size, but suspensions of these particles are difficult to deposit precisely on a surface, where inter-particle interactions affect plasmonic resonance. In contrast, top-down silver film patterning techniques such as nanosphere lithography, microcontact printing, and solid state superionic stamping allow for control of large arrays of particles in applications as a transparent conductors and for light trapping in photovoltaics.\footnote{73, 4, 74, 75, 76, 77, 56} Moreover, silver substrates with a wide variety of colors have also been demonstrated in films with focused ion beam (FIB) milled holes and slits.\footnote{78, 79} In addition to color filtering applications, silver structures have a wide variety of uses including plasmonic trapping, surface enhanced Raman spectroscopy (SERS), and plasmonic focusing.\footnote{80, 81, 82, 83}

Direct writing processes have the advantage of localized deposition, reduced number of process steps, and greater flexibility. Focused electron beam-induced deposition (FEBID) and focused ion beam-induced deposition (FIBID) are two prominent methods for localized metal deposition, where a precursor gas is adsorbed onto a substrate and subsequently decomposed by a charged particle beam. The vacuum chamber must be fitted with an insertion needle in order to introduce the gaseous precursors into the chamber
close to the deposition area. Since precursors must have a sufficient vapor pressure to flow into the chamber, selection of the appropriate material can be challenging and precursors are often organometallics such as metal carbylons or halogenophosphines. A review by Botman highlights the difficulty in depositing pure metals, with deposited material consisting of small metal clusters in an amorphous carbon matrix. Even more challenging is the lack of volatile precursor compound for silver.

An alternative to gas phase deposition is to inject a liquid silver precursor directly onto the substrate in a vacuum chamber. Bresin produced aqueous silver nitrate at low pressure through hydration of solid precursor particles or with direct droplet injection. While these techniques produced silver traces down to 70 nm in width, beam scattering caused by penetration through the liquid layer limited patterning to the small area where the liquid layer is thinnest. Even with the use of surfactants to produce a small contact angle, high resolution patterning is limited to the few microns around the perimeter of the droplet. Ocola has demonstrated similar deposition from aqueous silver nitrate using a thin polyimide membrane to contain the liquid. Though this configuration allows flexibility in the placement of silver, the technique resulted in granular silver traces with significant non-specific deposition. Both of these techniques for producing a liquid precursor within a vacuum environment significantly increase the complexity of the process, while achieving modest success.

In contrast to both gaseous and liquid based precursors for direct writing of silver nanostructures, this work investigates an all-solid-state writing process that uses a solid-state ionically conductive substrate to supply silver by electrochemical extraction. Several silver compounds are known to have high room temperature ionic conductivity, most notably $\text{RbAg}_4\text{I}_5$.[34] However, the rapid decomposition of the material in the presence of moisture makes its use as a substrate material impractical. Several silver oxyacid based compounds of the form $\text{AgI}_x(\text{Ag}_y\text{MO}_z)_{1-x}$ where $M=P$, As, Se, Te, Cr, Mo, and W have been found to be ionic conductors and are significantly less reactive to moisture compared to $\text{RbAg}_4\text{I}_5$. In particular, the structure and tunability of the glass transition, activation energy, and ionic conductivity of $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ glass mixtures have been well studied due to the wide transparent glass forming region from $x=0-0.6$. Addition of AgI to AgPO$_3$ increases the ionic conductivity.
from \(4.2 \times 10^{-6} \, \text{S cm}^{-1}\) for \(\text{AgPO}_3\) to \(3.2 \times 10^{-2} \, \text{S cm}^{-1}\) for \(\text{AgIAgPO}_3\) while the both glasses remain electrical insulators.[39] In this work, the superionic conductor \(\text{AgIAgPO}_3\) was chosen to demonstrate the efficacy of an electron beam to extract silver from an ionically conductive substrate. To highlight the importance of ionic conduction to the process, the much less conductive glass \(\text{AgPO}_3\), which is structurally similar to \(\text{AgIAgPO}_3\), was also characterized.(See Supplementary Information for additional background information on the \((\text{AgI})_x(\text{AgPO}_3)_{1-x}\) system). The process presented results in modification of the glass surface composition, producing a rich color palette with high lateral resolution and with potential applications for storage media and product authentication. With increased electron fluence, we also demonstrate the capability to direct-write silver nanoparticles of various shapes on a transparent substrate.

5.2 Silver Particle Generation in Glass

Silver doped glasses have been shown to locally precipitate silver when subjected to excitation such as that from femtosecond lasers, gamma rays, and electrons when followed by thermal annealing.[93, 94, 95, 96] After femtosecond direct laser writing (DLW) and heat treatment, silver doped zinc phosphate glass displays increased optical absorption below 450 nm due to the generation of several silver species and white fluorescence due to the development of \(\text{Ag}^{x+}_m\) nanoclusters.

In this process, the amplitude of the emission is proportional to the number of pulses applied and emission intensity-based multibit data storage has been demonstrated.[97] Bourhis describes the progression of this photochemical process in three steps. First, multi-photon absorption results in electrons elevated from the valence to conduction band within the matrix creating electron-hole pairs which are quickly captured by silver ions to form both neutral and charged silver species such as \(\text{Ag}^0\) and \(\text{Ag}^{2+}\) via the reaction shown in Equation 5.1. Second, silver nanoclusters of \(\text{Ag}^{x+}_m\), where \(m < 20\) and \(x < m\), are formed near the periphery of the treated area through a localized oxido-reduction clustering reaction shown in Equation 5.2. Finally, Ostwald ripening of the charged silver nanoclusters enlarges them to nanoparticles ranging from 5-15 nm.[98, 99] Due to the low room temperature diffusion
Figure 5.1: Schematic of the silver writing process. a) An electron beam scans the surface of the glass, with electrons depositing below the surface. Silver ions migrate to the deposition site neutralizing the charge buildup. b) Initially primary electrons generate electron-hole pairs which combine with local $\text{Ag}^+$ ions to form silver nanoparticles. Once the primary electron loses energy it also causes precipitation by reducing silver. c) When silver nanoparticles coalesce into a metal film thick enough to absorb the beam, film growth is only due to the absorbed electrons which drive electrochemical deposition.

of silver species in these glasses however, this final step requires extended heating by the laser or a separate heat treatment near the glass transition.

\[
2\text{Ag}^+ + e^- + h^+ \rightarrow \text{Ag}^{2+} + \text{Ag}^0 \tag{5.1}
\]

\[
\text{Ag}^+ + \text{Ag}^0 \rightarrow \text{Ag}_2^+, \quad \text{Ag}^+ + \text{Ag}_m^x \rightarrow \text{Ag}_{m+1}^{x+1} \tag{5.2}
\]

Direct e-beam writing on an ionic conductor shares several similarities as well as an important distinction from the DLW process. Figure 5.1a shows an overview of the process, where the beam from a high resolution scanning electron microscope (HRSEM) creates an interaction volume of mobile electrons in the substrate. Besides the energy associated with the beam, it also transfers a net current to the sample which is determined by the difference between the primary beam current and losses of secondary and backscattered electrons to the chamber. In the initial stage shown in Figure 5.1b, scattering of the primary beam generates secondary electrons which facilitate the creation of silver nanoclusters throughout the interaction volume, in a reduction and clustering process similar to DLW. However unlike the DLW process, the higher mobility of $\text{Ag}^+$ ions permits nanoparticle forma-
tion across the entire interaction volume, and not only at the boundaries. Moreover, the net negative charge deposited by the beam reduces the charge on particles and directly contributes to silver reduction as shown in Equation 5.3 resulting in increased silver deposition. Importantly, the high ionic conductivity of the substrate prevents surface charging by allowing $\text{Ag}^{+}$ ions migrate to the surface. As sufficient silver particles precipitate, they coalesce to form a film on the glass surface. When the film grows thicker than the beam penetration depth, as shown in Figure 5.1c, secondary electrons are no longer generated in the glass, and only direct silver reduction continues. At this point, further silver precipitation is restricted to the silver-substrate interface, which results in both vertical and lateral growth of the silver film.

$$\text{Ag}_m^x + e^- \rightarrow \text{Ag}_m^{x-1}$$ (5.3)

5.3 Silver Painting

Figure 5.2a depicts the color induced in patterned areas of $\text{AgIAgPO}_3$ with varying accelerating voltages and electron fluence. At each voltage from 1 kV to 12 kV, a gradient of primary beam fluence was applied from 0-2500 pC $\mu$m$^{-2}$. At 1 kV, the large secondary electron emission of the beam causes a net positive charge to be deposited, resulting in no reduction of colored silver. At 2 kV, the electrons emitted from the surface nearly match those of the incoming beam, resulting in limited formation of silver nanoclusters. For 3 kV and above, the charge of the incoming beam exceeds the emitted charge, resulting in net deposition of electrons and the electrochemical reduction of silver. From left to right, the increasing fluence results in a shift in hue. After a point, the patterned area loses saturation which is hypothesized to be due to the coalescence of isolated nanoparticles into a metallic film on the surface. Since higher voltage beams result in a wider range of electron penetration depths, higher fluence is required to achieve coalescence at high voltages. The color seen at low fluence was observed to sweep the visible spectrum with increased acceleration voltage, suggesting either a difference in initial nanoparticle nucleation size, particle concentration, or alteration of the glass index near the surface due to beam energy.

For comparison, Figure 5.2b shows patterning performed on a non-superionic
Figure 5.2: Color palettes produced on AgIAgPO$_3$ by electron beam irradiation. a) Optical image of AgIAgPO$_3$ patterned in a linear fluence gradient from left to right from 0-2500 pC $\mu$m$^{-2}$. From bottom to top the beam voltage is 1-12 kV. b) Image of AgPO$_3$ patterned in identical conditions showing dendritic growth and limited color palette. Scale bars are 10 $\mu$m.
Figure 5.3: Reflection Spectra of E-beam Patterned Dots. a) Total reflection spectra from dots patterned at 300 pC $\mu$m$^{-2}$ and several voltages. Data is offset vertically for clarity. b) Optical images corresponding to the 225 $\mu$m diameter dots.

Sample of silver metaphosphate. Whereas AgIAgPO$_3$ possesses a high room temperature ionic conductivity, the conductivity of AgPO$_3$ is four orders of magnitude smaller. Without adequate bulk conductivity, trapped charges accumulate during irradiation, resulting in long-lived charge trapping in the exposed areas and the development of a large electric potential between glass surface and the grounded stage to which it is attached. Doi and Asakura have demonstrated that in an electric field of 400-600 V cm$^{-1}$, AgPO$_3$ will undergo dielectric breakdown and grow silver dendrites though the bulk of the glass.[100] Indeed, AgPO$_3$ samples demonstrated dendritic growth of silver when subjected to 2-12 kV beams, which result in a net negative charge transferred to the glass. The reduction of silver in the growth of uncontrolled dendrites consumes the surface charge, lowering the overall nanoparticle growth in the interaction volume. Moreover, the preference towards dendrite growth is accentuated in AgPO$_3$ due to the limited availability of Ag$^+$ ions near the surface compared to further in the bulk. The net result is the extremely limited color profile when compared to irradiated AgIAgPO$_3$. At high fluence, the penetration of the silver dendrites into the glass matrix generated enough stress to fracture the surrounding glass.

Specular data, shown in Figure 5.3, was gathered from larger dots pat-
Figure 5.4: Microscope optical images on AgIAgPO$_3$ produced by patterned electron beam irradiation. a) Optical image of high-contrast bicolor graphic. Patterned in two passes: 5 kV and 7 kV $V_{\text{acc}}$. b) Optical image of gradient painting pattern in two passes: 3 kV and 6 kV $V_{\text{acc}}$. Scale bars are 25 $\mu$m.

Patterned in AgIAgPO$_3$ with an electron fluence of 300 $pC \mu m^{-2}$. Dots were 225 $\mu m$ to provide sufficient signal to collect specular data. The combined diffuse and specular reflection spectra show that at 3 kV, very little alteration is made in the visible range at this fluence. Beginning at 4 kV, the yellow color is revealed to be a pair of broad peaks in reflection appears across the visible range. This is in contrast to the extinction below 450 nm by the DLW process and the single fluorescence peak associated with it. With further increase in acceleration voltage, the spectrum remains qualitatively the same, but shifted towards longer wavelengths. This is consistent with the extracted silver resulting in a continuous change in the effective refractive index of the top layer along with increase in electron absorption depth with beam voltage.

Figure 5.4 demonstrates different approaches to patterning utilizing the available color palette. In Figure 5.4a, a high contrast bicolor optical image was produced using beams at 5 kV and 7 kV at fluences of 440 $pC \mu m^{-2}$ and 477 $pC \mu m^{-2}$ respectively. This method produces uniform colors over large areas and can produce vibrant sub-micron colored lines. Alternatively, in Figure 5.4b the image was produced using several levels of fluence from beams.
5.4 Silver Film Growth and Surface Properties

Across all electron fluences, the surface became raised in the patterned areas. Figure 5.5 shows the results of writing bulk quantities of silver in the form of 4\(\mu m \times 4\mu m\) and 2.5\(\mu m \times 2.5\mu m\) squares, while varying accelerating voltage between 5 kV, 7 kV, and 10 kV. For each accelerating voltage, the electron fluence was set by varying the writing duration of the beam while at constant current. For doses up to 3-5 \(nC \mu m^{-2}\), the thickness increased monotonically, with higher acceleration voltages resulting in faster deposition rates. Beyond 3-5 \(nC \mu m^{-2}\) the growth rate transitioned to a lower, linear rate of 0.012 \(\mu m^3 nC^{-1}\), 0.028 \(\mu m^3 nC^{-1}\), and 0.039 \(\mu m^3 nC^{-1}\) for voltages of 5 kV, 7 kV, and 10 kV respectively. The clear decrease in film growth rate indicates a change in the dynamics of deposition. This is consistent with the notion that once a thick layer of silver coats the substrate, secondary electrons generated in the silver are reabsorbed before reaching the underlying glass, causing the deposition rate only to be driven by the charge absorbed by the silver film. In the high fluence regime, variation in deposition rate with acceleration voltage is consistent with lower total emitted electron efficiency at higher voltages.

The transition to a film of silver atop the glass substrate from subsurface nanoparticles is shown in Figure 5.5b,c. Morphologically, the writing process began with a uniform increase in surface height without large increases in surface roughness. As electron fluence was increased, silver grains became visible on the surface and coalesced to form a continuous metal film. The height at which grains became visible varied with acceleration voltage, where low voltage beams produced grains at the lowest fluence. This is consistent with Monte Carlo simulations which predict a widening of electron penetration distributions with increased acceleration voltage. While lower energy beams concentrate the initial silver deposition closer to the surface, high energy beams distribute silver deposition over a wider range of depths, requiring a higher fluence for the concentration of silver at the surface to reach...
Figure 5.5: Silver growth with increasing electron fluence. a) Graph of thickness vs dose, b) AFM image of squares patterned at 5 kV from 0.5-21.3 nC µm$^{-2}$, c) RMS roughness vs thickness. Moving average lines added to aid the eye. Scale bar is 10 µm.
Figure 5.6: High resolution silver structures patterned on AgI\(\text{AgPO}_3\). a) Lateral resolution test of lines written at 5 kV and 3.9 \(nC \mu m^{-1}\). b) Silver lines patterned with a 50 nm gap. c) Bow tie antennae with 55 nm gap. d) 150 nm NSOM aperture in 280 nm thick silver film. Scale bars 1 \(\mu m\), inset scale bar 100 nm.

the coalescence threshold.

AFM measurements also show an increase in the lateral size of patterns compared to the nominal dimensions. While some of this increase is due to the scattering effects of the beam within glass, features continue to spread even when the silver film is thick enough to absorb the beam. Since creation of thick films is driven electrochemically, deposition is not localized to the beam but to the entire area of the silver film, uniformly increasing film thickness.

Figure 5.6a demonstrates the lateral resolution of lines written at 5 kV and 3.9 \(nC \mu m^{-1}\). Lines are 160 nm thick, and 400 nm wide. At fluences above the transition to purely electrochemical deposition, pattern edges gain sharp contrast. Though beam scattering appears to limit the minimal achievable
line width, the process displays much higher resolution in producing silver gaps. Since patterns grow laterally in the electrochemical regime, features can be grown such that gaps reach less than 60 nm. Figure 5.6b-d demonstrate structures spaced 50 nm apart, a bowtie antennae with a thickness of 215 nm and a gap of 55 nm, and a 150 nm NSOM aperture produced in an opaque 280 nm thick silver film. All non-patterned areas remain optically transparent.

5.5 Thermal Analysis

In addition to initiating silver nanoparticle precipitation, the electron beam delivers thermal energy to the glass surface which may affect the process. Hiki, Takahashi, and Kogure measured the thermal conductivity at 40°C of AgPO$_3$ and AgIAgPO$_3$ to be only 0.430 W m$^{-1}$ K$^{-1}$ and 0.259 W m$^{-1}$ K$^{-1}$ respectively, which suggests that heat may be poorly transferred away from the interaction volume, especially under high current patterning.[47] To estimate the expected steady state temperature rise created by the electron beam, a 2D axisymmetric finite element model of the glass was made in COMSOL. The relevant glass domain modelled as a 10 μm radius by 10 μm deep cylinder modeled with a thermal conduct. Due to the increased absorption and higher thermal conductivity of silver during the process, a third simulation was conducted assuming the interaction volume consists of silver with AgIAgPO$_3$ as the surrounding material. Boundary conditions at the sides and base of the model were fixed at 20°C, while the top surface was assumed to be thermally insulating.

Simulations were conducted for 3 nA beams corresponding to 5 kV, 7 kV, and 10 kV acceleration voltages. Heat generation from the electron beam interaction was assumed to be uniform within a hemispherical interaction volume. Total beam power was calculated in Equation 5.4 as a function of the energy carried by the each electron and the primary beam current. The effective beam heating power can be calculated by considering the energy lost due to escaped secondary electrons as well as the slightly reduced energy carried away by backscattered electrons. However, the energetic contribution of lost secondary electrons is small, and the majority of backscattered electrons retain a significant portion of their initial energy. To simplify
Table 5.1: Summary of thermal beam power and resulting maximum temperatures from finite element simulation. Backscatter efficiency and maximum penetration depths calculated from Monte Carlo simulations.

<table>
<thead>
<tr>
<th>Beam Accelerating Voltages</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 kV</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Primary Beam Power at 3 nA, $\mu$W</th>
<th>15.0</th>
<th>21.0</th>
<th>30.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Backscatter Efficiency, $\eta$</td>
<td>0.269</td>
<td>0.262</td>
<td>0.28</td>
</tr>
<tr>
<td>$\text{AgPO}_3$</td>
<td>0.335</td>
<td>0.328</td>
<td>0.35</td>
</tr>
<tr>
<td>$\text{AgIAgPO}_3$</td>
<td>0.364</td>
<td>0.368</td>
<td>0.390</td>
</tr>
<tr>
<td>Approximate Penetration Depth, nm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{AgPO}_3$</td>
<td>300</td>
<td>525</td>
<td>1000</td>
</tr>
<tr>
<td>$\text{AgIAgPO}_3$</td>
<td>250</td>
<td>450</td>
<td>750</td>
</tr>
<tr>
<td>Ag in $\text{AgIAgPO}_3$</td>
<td>120</td>
<td>200</td>
<td>360</td>
</tr>
<tr>
<td>Thermal Dissipation Power density, x $10^{13}$ W m$^{-3}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{AgPO}_3$</td>
<td>19.4</td>
<td>5.11</td>
<td>1.03</td>
</tr>
<tr>
<td>$\text{AgIAgPO}_3$</td>
<td>30.5</td>
<td>7.39</td>
<td>2.64</td>
</tr>
<tr>
<td>Ag in $\text{AgIAgPO}_3$</td>
<td>264</td>
<td>79.2</td>
<td>18.7</td>
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<tr>
<td>Maximum Temperature, $^\circ$C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{AgPO}_3$</td>
<td>39.9</td>
<td>35.8</td>
<td>31.2</td>
</tr>
<tr>
<td>$\text{AgIAgPO}_3$</td>
<td>56.2</td>
<td>48.1</td>
<td>42.9</td>
</tr>
<tr>
<td>Ag in $\text{AgIAgPO}_3$</td>
<td>68.4</td>
<td>60</td>
<td>50.2</td>
</tr>
</tbody>
</table>

Calculations, the effective beam heating power was calculated using Equation 5.5 by assuming backscattered electrons retained their initial energy. The backscattering coefficient, $\eta$, as well as the maximum penetration depth were obtained from Monte Carlo simulations and are shown in Table 5.1.

$$P_{\text{total}} = \frac{E_{\text{electron}} I}{1.6 \times 10^{19} \text{C/e}^-} \quad (5.4)$$

$$P_{\text{thermal}} = (1 - \eta) P_{\text{total}} \quad (5.5)$$

Figure 5.7 illustrates that since the glass was thermally insulating, heat was well confined to the interaction volume while the rest of the simulated volume remained near room temperature. The maximum temperatures in simulations of $\text{AgIAgPO}_3$ were 56.2$^\circ$C, 48.1$^\circ$C, and 42.9$^\circ$C, all below the glass transition temperature of the substrate. With a higher thermal conductivity and larger interaction volume, maximum temperatures reached in $\text{AgPO}_3$ are even lower. Considering that silver precipitation in the glass is likely to increase the thermal conductivity in the interaction volume, it seems likely that the electron beam thermal interaction with the glass does not significantly the process at the beam powers investigated.
Figure 5.7: Finite element model of heating in AgIAgPO$_3$. Example simulation of the steady state temperature rise due to thermal input from electron beam. The simplified thermal modelling assumes uniform power dissipation a hemispherical interaction volume. With a 7 kV beam at 3 nA, there is less than a 28°C temperature rise. Since this is still well below the substrate glass transition temperature of 81°C, the process does not induce large scale melting during irradiation.
Table 5.2: Energy-Dispersive X-ray Spectroscopy of AgIAgPO$_3$, E-beam extracted material, and Bulk Ag reference

<table>
<thead>
<tr>
<th></th>
<th>Ag [at %]</th>
<th>I [at %]</th>
<th>P [at %]</th>
<th>O [at %]</th>
<th>C [at %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgIAgPO$_3$</td>
<td>38.6</td>
<td>19.8</td>
<td>20.5</td>
<td>14.0</td>
<td>7.1</td>
</tr>
<tr>
<td>Extracted Ag</td>
<td>88.1</td>
<td>0.2</td>
<td>1.3</td>
<td>1.3</td>
<td>9.1</td>
</tr>
<tr>
<td>Bulk Ag</td>
<td>88.7</td>
<td>0</td>
<td>0</td>
<td>0.4</td>
<td>10.9</td>
</tr>
</tbody>
</table>

5.6 Material Analysis

Energy-dispersive spectroscopy (EDS) was conducted on the glass before and after patterning at high fluence, with the results shown in Table 5.2. For reference, the spectrum of pure silver was measured as well as that of AgIAgPO$_3$. Due to carbon contamination in the chamber, a small amount of carbon was detected in all samples. To measure the glass prior to deposition, the spectrum of the glass was recorded at low magnification, reducing the electron fluence during measurement to a negligible level. The unpatterned glass displayed strong silver, iodide, and phosphorous peaks, matching the expected ratios for AgIAgPO$_3$. Compared to the unpatterned glass, areas of glass patterned at 10 kV show more silver present, with iodide, phosphorus, and oxygen content suppressed. Chamber contamination, however, causes carbon content to rise slightly with increased beam dwell time. Unlike EBID deposition with carbon containing precursors, the carbon content of structures made in this process can be reduced through better chamber maintenance.

5.7 Conclusion

The effects of electron beam irradiation of a high ionic conductivity transparent glass, AgIAgPO$_3$ was investigated. The electron beam initiates precipitation of silver within the beam interaction volume leading to swelling of the surface. It was found that for fluences lower than 2500 $pC \mu m^{-2}$ the surface exhibits strong coloration throughout the visible range. Though several papers have shown color change of phosphate glasses containing silver after local excitation, this is the first time such a change has been demonstrated that smoothly sweeps the entire visible range and requires no subsequent
heat treatment. We attribute the immediate appearance of color to silver nanoparticle formation facilitated by the high room temperature mobility and concentration of Ag$^+$ ions present in AgIAgPO$_3$, in conjunction with direct injection of charge from the beam. Without high ionic conductivity, irradiation of AgPO$_3$ glass only produces a limited set of colors.

From AFM scans of the surface, surface modification due to the electron beam initially appeared as a raised surface with the process capable of fine control of surface height down to 1 nm average surface height for low fluence ($< 300 \text{ pC } \mu \text{m}^{-2}$ at 5 kV). At sufficient electron fluence, the accumulated embedded silver particles coalesced into a film and break through to the surface. Thick film formation of greater than 1m for high fluence (3000 $\text{ pC } \mu \text{m}^{-2}$ at 10 kV) was possible by electron capture and subsequent electrochemical growth of silver particles on the surface. Both the colored embedded silver nanoparticles and silver film on the surface were patterned in submicron features, with surface patterning displaying line width resolution of 400 nm and feature-to-feature spacing of less than 100 nm. Film growth characteristics were consistent with Monte Carlo simulations indicating that the process is controlled by both the energy and charge absorbed by the substrate from the electron beam.

This process displays several favorable characteristics for future applications. The patterns generated here may find use for high resolution color applications including optical data storage and color security labeling, or systems requiring fine control of surface height. The ability to tailor silver nanostructures is especially suited to plasmonic applications requiring optically transparent substrates. Future work includes exploring similar glass compositions, and optimizing for environmental stability of both the glass and written structures such that high reliability, long term patterning is practical.

5.8 Experimental Section

The glass, AgIAgPO$_3$, was synthesized from reagent grade silver nitrate (99.995% from Salt Lake Metals), monobasic ammonium phosphate (99.99% from Sigma Aldrich) and silver iodide (99.9% from Alfa Aesar). First, stoichiometric amounts of silver nitrate and ammonium phosphate were heated
slowly in an alumina crucible until the liquid finished giving off fumes, at
which point the crucible was heated to 600°C for one hour. Next, the silver
metaphosphate was quenched on an aluminum plate, before being mixed in
a new alumina crucible with equimolar amounts of silver iodide at 600°C
for one hour. Afterwards, the glass melt was soaked in a borosilicate tube
at 400°C for 24 hours to remove particles generated from the glass reaction
with the alumina crucible. After slow cooling, the glass was melted on an
aluminum holder that was previously sputtered with a 100 nm layer of silver
to act as a sacrificial counter electrode to the electron beam. Flush with the
base of the ring is an optical window, which allows illumination from below.
A flat surface for patterning was created by melting the convex surface of
the glass against an optical flat, cooling and separating the two parts. Sil-
ver metaphosphate was separately melted onto silver foil to provide a control
sample of low ionic conductivity glass. Writing was performed on a FEI Dual
Beam 235 FIB using the electron column, with accelerating voltages ranging
from 1-12 kV. A faraday cup was used to measure the beam current prior to
each pattern, and the write time was adjusted to achieve the desired electron
fluence. The beam currents for 1 kV and 2 kV were 980 pA and 1800 pA
respectively, and beam currents for 3-12 kV acceleration were measured to
range from 2.9 nA to 3.9 nA. Height data and AFM images were produced
with an Asylum Cypher in tapping mode. Elemental analysis was performed
on a JOEL JSM-6060LV scanning electron microscope with an Iridium Ultra
EDS system from iXRF Systems. The bulk silver reference was a 99.99% sil-
ver pellet obtained from Kurt J. Lesker. Optical images were recorded with
an optical microscope with maximum NA=0.55, a Canon Rebel T3i using
illumination from a high intensity halogen lamp, and a polytetrafluoroethylene
disk for white balance calibration. Reflection spectra were obtained with
a Cary 5000 UV-VIS-IR spectrophotometer using an integrating sphere with
a 200 μm diameter black aperture to mask all but the patterned area.
6.1 Introduction

Controlling micro-scale reflection and transmission properties are fundamental to both display and optical storage technologies. Structural color from silver and aluminum nanostructures have demonstrated a wide color palette for filtering in both transmission and reflection through plasmonic tuning. Extraordinary transmission through nano-scale hole arrays can be tuned by varying hole size and spacing to filter light.\[101, 102, 79\] In reflection, a wide range of colors are possible from metal-coated pillars.\[103, 104, 105\] However, since the color-generating plasmonic resonance of these structures is highly sensitive to the geometry, these structures are typically fabricated using an expensive, multi-step e-beam lithography process or through relatively slow focused ion beam milling to achieve tight dimensional tolerances.

In comparison, coloration due to silver nanoparticles embedded in a dielectric can be better controlled through the precise growth conditions of the particles. Addition of silver to the material can be achieved through silver ion diffusion from a salt bath, as well as plasma-generated silver ion implantation.\[106, 107, 108, 109, 110, 111, 112\] These processes, however, are limited to large areas and result in a single color. Additionally, the plasmonic absorption of these substrates lies from 390-420nm, generally producing a yellow hue. A more flexible approach uses femtosecond laser irradiation of Ag-doped phosphate glass, and permits patterning with nanoparticle formation occurring in subsequent thermal treatment.\[108, 99, 97\] However, the limited silver dopant and charge neutral process limits the quantity of reduced silver within the material.

Recent reports have demonstrated reflective color generation from electron irradiated AgIAgPO₃, creating a wide range of colors in reflection.\[51\]
Unlike colored substrates produced using plasmonic pillars, this process can be completed in a single processing step, without e-beam resists or a separate metal deposition process. Moreover, the patterning itself can occur in a conventional SEM with lithography package.

In this work we expand upon this color patterning process, examining the role of process parameters as well as substrate composition in the final coloration produced. The range of colors produced from \((\text{AgI})_x(\text{AgPO}_3)_{1-x}\), for compositions of \(x=0-0.5\), is explored for a series of primary beam fluences and electron energies. Time dependent processing parameters, including beam current and beam dwell time, are also varied to examine their impact. Finally, enhanced patterning methods using multiple e-beam voltages are explored to further expand the color palette as well as demonstrate color erasing.

6.2 Experimental

\(\text{AgPO}_3\) glass was synthesized from \(\text{AgNO}_3\) (99.995% purity from Salt Lake Metals) and \((\text{NH}_4)\text{H}_2\text{PO}_4\) (99.99% from Sigma Aldrich) by heating in an alumina crucible to 500°C until no further gas evolved, and then quenched on an aluminum plate. To produce \((\text{AgI})_x(\text{AgPO}_3)_{1-x}\) where \(x=12.5\%, 25\%, 37.5\%\) and 50%, appropriate ratios of \(\text{AgPO}_3\) were mixed with \(\text{AgI}\) (99.9% purity from Alfa Aesar) in separate alumina crucibles and heated to 600°C for one hour, then transferred to borosilicate tubes where the glasses were allowed to soak at 400°C for 60 hours before cooling to room temperature.

Two types of samples were produced depending on whether transparency was required for analysis. For thin film glass substrates, the glass was melted onto silver foil with polyimide tape to serve as a spacer while a blade was wiped across the surface. The tape was then removed before cooling to room temperature. The thin layer of glass produced in this manner was approximately 60 microns thick. For transparent substrates, 2 mm thick aluminum rings were DC magnetron sputtered with 120 nm of silver to serve as a non-blocking counter electrode. \((\text{AgI})_x(\text{AgPO}_3)_{1-x}\) glass was then melted into the rings and sandwiched between microscope slides which were removed upon cooling.

Electron beam patterning was performed on an FEI Dual Beam 235 FIB.
using the electron column, with the primary beam current measured using a faraday cup prior to patterning. Optical images were taken on a Canon T3i DSLR camera or with a Lumenera Infinity2-5C camera. Optical properties of the glass were measured with a Varian Cary 5000 UV-VIS-IR spectrophotometer and a J.A. Woollam VAS Ellipsometer.

6.3 Results and Discussion

6.3.1 Compositional and beam voltage effects

As described previously, the process of color production in \((\text{AgI})_x(\text{AgPO}_3)_{1-x}\) requires ionic conductivity of the substrate to be able to extract additional silver at the surface.[51] Fundamentally, the ionic conductivity must also be sufficient enough to prevent surface charging and the associated dendritic growth of silver. In Figure 6.1, thin film substrates with compositions of \((\text{AgI})_x(\text{AgPO}_3)_{1-x}\) ranging from \(x=0-0.5\) are patterned to compare the effect of silver ion conductivity on the process. For each glass substrate and accelerating voltage, the electron beam is scanned in a single pass from left to right with varying dwell time to establish a linearly increasing fluence from 0-12.5x10^4 \(\mu\)C/cm^2. Each strip is patterned at a single beam voltage with acceleration voltages of 1-12 kV explored. Where there is no silver iodide, \(x=0\), silver metal is generated instead of color gradients, and show the beginnings of dendritic growth from the edge of the pattern. Interestingly, the onset of bulk silver precipitation is delayed until a fluence of 1.25-3.50 x10^4 \(\mu\)C/cm^2. This is likely due to the depletion of locally available silver for reduction, which initiates surface charging. At 1 kV, where the net current to the surface is positive, AgPO_3 exhibits a strong white luminescence not seen in other glasses.

With the addition of just 12.5% AgI, color is produced on the substrate, though with a limited range of colors. These colors appear similar to that seen from femtosecond laser irradiation.[99] The low variability with beam voltage and fluence allows robust control of color production. Similar patterning on glass with AgI content of 25% results in a wider range of colors, where the entire color range found for 3-12 kV patterning in the 12.5% glass is present in the smaller 3-6 kV process window. Likewise, the color range found from
Figure 6.1: Color palette exploring different substrate compositions, e-beam acceleration voltages, and fluence. Sample is a thin film of $(AgI)_x(AgPO_3)_{1-x}$ on silver foil. Each column explores the reflective colors found when patterning $(AgI)_x(AgPO_3)_{1-x}$ substrates where $x=0-0.5$. Each horizontal bar represents a linear gradient of increasing primary beam fluence from $0-12.5 \times 10^4 \, \mu C/cm^2$ going left to right respectively. Within each column, each bar is patterned using a single beam voltage, ranging from 1kV to 12 kV. Increasing AgI content in the substrate progressively increases the range of possible colors. Dotted lines are included to guide the eye to the trend of varying color palette between substrates. Scale bar is 50 microns.
patterning glass with 37.5% AgI is wider still, and contains all the colors found for 3-12kV patterning of 25% AgI glass compressed to a processing window of 3-7kV. Patterning of AgIAgPO$_3$ can produce the widest color palette, expanding upon the color palette of 37.5% glass for beams greater than 8 kV. The dotted lines on Figure 1 are included to help guide the eye to the trend of similar colors observed between substrates of different AgI content.

A side effect of the compositional change from x=0-0.5 is the increase in backscattering efficiency for glasses with higher silver and iodine content. Combined with secondary electrons lost from the sample surface, at low voltages the direction of net charge flow in the sample is reversed. Since current reversal eliminates the reducing effect on silver ions, patterning at or below 1kV for 12.5% and 25% glass compositions, and at or below 2 kV for compositions of 37.5% and 50% fails to generate color.

Though the reduction of silver to silver metal is evident from high fluence irradiation[51] color generation occurs at lower electron fluence such that the reduced silver is too small to directly observe in optical or scanning electron microscopes. One hypothesis is that the silver forms nanoscale clusters at low fluence, and these can resonate plasmonically to produce the observed colors. Alternatively, the large quantities of Ag$^0$ and non-resonant Ag$_{en}$ clusters in the glass may locally shift the refractive index, leading to thin film interference between the patterned area and the underlying bulk substrate. Though the ionic conductivities of the examined glasses constitute the primary difference between glasses with different silver iodide content, Figure 6.2 demonstrates that there is also a large variation in optical properties between substrates. The transmission through 2 mm samples of (AgI)$_x$(AgPO$_3$)$_{1-x}$ glass, normalized to the transmission at 1000 nm is shown in Figure 6.2a. AgPO$_3$ remains largely transparent into the ultraviolet range, whereas even 12.5% AgI content results in strong absorption in that range. Higher AgI content shifts the cutoff frequency further into the visible spectrum. Figure 6.2b-c plots the refractive index of the glasses as measured by spectroscopic ellipsometry, highlighting the strong dependence of the real component upon AgI content, varying the index from 1.67 to over 2.2 in the visible region. Moreover, the shift in absorption can be seen to be simultaneous with an increased and shifted resonance from the UV to visible spectrum. Since both plasmonic resonance and thin film color effects depend upon the substrate
Figure 6.2: Optical properties of (AgI)_x(AgPO_3)_{1-x} glass. a) Transmission spectrum as measured by spectrophotometer, normalized to transmission at 1000nm. b-c) Real and imaginary parts of refractive index calculated from spectrographic ellipsometry. Legend is for all three plots.
Figure 6.3: Extended patterning parameters for AgIAgPO$_3$. Beam voltages from 10-30kV, with linear fluence gradient from 0-100x10$^4$ $\mu$C/cm$^2$. Scale bar is 50 microns.

refractive index, the large shift in refractive index between glass compositions will significantly factor in the results of this process, regardless of the source of color generation.

6.3.2 High voltage

Figure 6.3 shows the effects of patterning AgIAgPO$_3$ with higher voltages up to 30 kV. Whereas traditional electron beam lithography uses electrons with 10-100 keV energy to achieve high edge contrast, the bulk patterning nature of this process does not benefit from high voltages. Instead, higher energy electrons increase the beam penetration depth and proximity effect based beam spreading. This larger interaction volume results in dilution of the injected charge, preventing visible color formation despite reduction of silver. Additionally, the increased thickness of the patterned volume significantly exceeds the depth of field during imaging, further preventing high contrast imaging of pattern boundaries.
6.3.3 Patterning process parameters

In direct electron capture, primary electrons from the beam are ultimately either captured by silver ions in the substrate which reduce to form Ag\(^0\), or are captured by silver metal clusters upon which further silver deposits. The combination of these processes result in a quantity of silver metal which is expected to be proportional to the charge delivered to the substrate. The quantity of silver reduced near the surface of the glass is thought to be the primary determining factor in the observed color after patterning.

To explore this relationship, identical fluence gradients were patterned at 5kV on AgIAgPO\(_3\) glass at currents of 0.35 nA, 1.43 nA, and 5.94 nA each in a single pass. Varying beam current is linked to the temperature rise associated with dissipating the electron energy. Since the thermal conductivity of the
glass is low, there can be a highly localized region of heating. However, this region typically remains below the glass transition temperature at the power levels investigated.[16] The similarity between the color gradients in Figure 6.4a demonstrate relative insensitivity of the process to thermal fluctuations since the material remains ionically conductive even at room temperature.

While the process so far has been generally described as time independent, some time-dependent behavior is displayed. In Figure 6.4b, identical fluence gradients were patterned at 5 kV and 1.43 nA on AgIAgPO$_3$, but with the patterning process broken into multiple raster passes where the beam dwell time per pass has been correspondingly shortened. There is a marked shift from the formation of a small range of intense colors for a single pass, to a less saturated but broader spectrum for multiple passes. Specifically, the use of multiple passes results in color at higher fluence ranges where only white is observed in single pass patterning. The mechanism for this change is still poorly understood, but is likely due to a shift from near steady state precipitation for long dwell times to one sensitive to initial conditions for shorter dwell times. Further study is required to better understand the role of local silver ion concentration in the nucleation and growth of the silver structures which determine the colors produced.

6.3.4 Optical transmission of patterns

Figure 6.5 also illustrates that patterns written on a transparent AgIAgPO$_3$ glass sample increase the optical density to the point of becoming opaque. Due to the charge sensitive nature of the substrate, direct non-destructive observation of nanoparticle size has proved challenging. However the opacity of patterned areas demonstrates that the structures formed though patterning are not purely dielectric since they are effective absorbers in transmission. Figure 6.5b analyzes the optical density of writing, showing that for linearly increasing fluence, there is a linear increase in optical density, opening up possibilities for greyscale patterning in transmission.
Figure 6.5: Optical transmission in patterned areas. a) Color transmission images of 0-20x10^4 µC/cm² fluence gradient patterned at 5kV, 7kV, and 10kV. Despite displaying colors in reflection, the patterned areas are opaque in transmission. b) Optical density increases linearly with fluence in 0-10x10^4 µC/cm² region. Limited image bit depth prevented measuring optical densities for higher fluence.
6.3.5 Image resolution

Previous work[51] has demonstrated that this process is capable of submicron color resolution in high contrast color images. The primary factor in determining the lateral resolution of color patterns is the interaction volume of scattered electrons generated by beam spreading within the substrate. Thus, while the size of the electron beam incident upon the substrate may be on the order of a few nanometers the ultimate resolution achievable is closer to the interaction volume—typically on the order of a few hundred nanometers—and should be dependent upon the beam-substrate interaction while independent of feature size. The spreading effect becomes the dominant area component for fluence calculations especially when patterning at submicron scales. However, due to the precise positioning possible with the beam it is possible to achieve higher resolution between adjacent patterns. Figure 6.6 investigates the patterning resolution of 1µm by 5µm bars patterned at 8x10^4 µC/cm^2 with nominal gap sizes ranging from 100-800 nm for beam accelerating voltages of 3 kV, 5 kV, 7 kV, and 10 kV. With each pattern receiving the same primary fluence, pattern width increases in size with higher beam energy. The gap between bars can be clearly resolved at 300nm for 3kV, 5kV, and 7kV patterning, whereas lines written at 10kV were resolvable only at 500nm. The decreased resolution at higher beam energies is attributed to the correspondingly larger interaction volumes, in conjunction with an increase in color variability which decreases the effective contrast.

6.3.6 Multi-step patterning

The color gamut demonstrated so far has focused on patterning at a single acceleration voltage, with the main process parameter being the total fluence. Addition of a second patterning at the same fluence serves to advance the resulting colors along the known color trajectory. However, the variation of beam penetration depth with accelerating voltage provides an opportunity to extend the total color palette through more complex layering of silver extraction. Figure 6.7 demonstrates the results of two stage patterning, exploring a large parameter space through the crossing of two independent linearly increasing dosage gradients: the first pattern increasing in fluence in the horizontal direction and second pattern increasing in the vertical direc-
<table>
<thead>
<tr>
<th>Nominal Gap Size</th>
<th>100 nm</th>
<th>200 nm</th>
<th>300 nm</th>
<th>400 nm</th>
<th>500 nm</th>
<th>600 nm</th>
<th>700 nm</th>
<th>800 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 kV</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 kV</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 kV</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 kV</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Figure 6.6: Optical resolution images for 3 kV, 5 kV, 7 kV, and 10 kV patterning at $8.0 \times 10^4 \mu C/cm^2$. Minimal proximity determined using 1 $\mu m$ x 5 $\mu m$ bars, separated by 100-800 nm gaps. Distinct bars are visible in 3 kV, 5 kV, and 7 kV patterns with 300 nm gaps, matching the expected maximum optical resolution of the microscope system used. At 10 kV, distinct bars are visible with a 500 nm gap. Scale bar is 5 microns.
tion. The extension of each individual pattern beyond the overlapped square region allows for comparison of each patterning stage to that of the combined region. To determine if the process is commutative, the patterning was repeated with the beam order reversed. As demonstrated in Figure 6.7b, the order of patterning plays a significant role in color generation. In instances where the higher voltage beam is followed by a lower voltage beam, all three combinations of 3 kV, 5 kV, and 7 kV share a similar result. Most combinations of the beams result in a range of light to dark shades of blue with higher fluences tending towards black before becoming highly reflective at the highest combined fluences. Since patterning at all but the lowest fluence produces an opaque layer, it is likely that the deeper penetrating first pattern is covered up by the second pattern. These multi-energy patterns also shift away from the color trajectory expected from a single, low-energy processing step due to the seeding of silver in the surface from the first processing step.

In instances where the lower energy beam is used first, a greater variety of colors is observed. As expected, in regions where the patterning fluence is very low, the color from the other pattern dominates the result. However, when either pattern is above 5 x10^4 µC/cm^2, a blending of colors occurs that produces a gold color in the 3 kV / 5 kV pattern or a unique magenta stripe in 3 kV / 7 kV patterns. These more nuanced combinations of beam energy and fluence expand the available color palette and potentially increase the color intensity, often at less a combined fluence than is possible when patterning is done in a single step. Figure 6.7c demonstrates on a larger area the generation of new colors through overlapping of two 48 m wide squares: the first patterned with 1.15 x10^5 µC/cm^2 at 3kV and the second subsequently patterned with 6 x10^4 µC/cm^2 by a 7 kV beam. This procedure outlines how new colors generated from crossed gradient experiments can be applied to discover patterning pairs which display high contrast when overlapped.

6.3.7 Erasing

The high energy electrons within the primary beam create a complex interaction within the substrate. These so called primary electrons can be deflected by close interactions the atomic nuclei of the substrate. Through successive interactions, some portion of these electrons can be completely change direc-
Figure 6.7: Effect of overlaying different patterning voltages. a) Two linear fluence gradients are patterned sequentially, each with a fluence ranging from 0-20x10^4 μC/cm². The overlapping region is 40 μm, with a 15 μm strip that is outside the overlapped region and demonstrates independently the colors produced by the individual patterning steps. b) Permutations of 3 kV, 5 kV, and 7 kV gradients. c) Using process parameters from part (b) at 3 kV and 7 kV to demonstrate a new color generated in a 32 μm wide overlapped square created from two 48 μm squares.
tion and end up leaving the substrate as so-called backscattered electrons. Since the interactions with the substrate are relatively elastic, backscattered electrons retain most of their energy. Alternatively, primary electrons can interact with the electrons in the substrate, knocking them out of their ground state and freeing them to move. However, these secondary electrons have low energy, below 50 eV, and through further interactions with the substrate quickly lose their energy. Because of this, most secondary electrons are recaptured within a few nanometers of their generation. Still, for secondary electrons generated near the surface, it is possible for secondary electrons to escape the substrate into the vacuum.

\[ I_s = (1 - \eta - \delta)I_p - \frac{dQ}{dt} \quad (6.1) \]

Equation 6.1 shows the overall charge conservation at the surface. Though surface charging is possible with insulating substrates, the ionic conductivity of the substrates presented here is sufficient to limit all but a small amount of charging. Therefore, the stage current \( I_s \), which is a direct measure of charge transferred to the substrate, consists of the primary beam current, \( I_p \) less the secondary and backscattered electron efficiencies. In general, backscattered electron efficiency tends to remain somewhat constant for electron energies above 10kV, depending primarily on the atomic number of the substrate. At such high energies, the vast majority of secondary electrons are generated at sufficient depth that most are recaptured within the substrate. At electron energies of a few kV however, the interaction volume remains near the substrate surface and secondary electron emission increases. Since a single primary electron possesses enough energy to generate many secondary electrons, the yield of secondary electron emission can exceed that of the incoming beam.

Figure 6.8 demonstrates the stage current to primary beam current on a reference of silver. This takes into account both the secondary electron efficiency as well as the backscattered efficiency. Above 10kV the ratio levels off, since both the backscattered and secondary electron efficiency do not vary much at higher energies. However, at approximately 2kV it can be seen that there is zero net current. Below this beam energy, there is positive charging of the surface. Writing of silver demonstrated above focuses on using beams with energy of at least 3kV where a net negative charge is transferred.
Figure 6.8: Stage current yield on silver. At above approximately 2kV, there is net transfer of electrons to the stage, but below this voltage the current reverses due to high secondary electron emission. Data taken at several magnifications to explore the potential effect of chamber contamination and associated carbon surface deposition.

to the substrate. For lower electron energy the ability to transfer a positive charge was hypothesized to have some oxidizing effect on silver nanoparticles, potentially erasing colors written through this technique. Since the transition from negative to positive charging depends upon both the secondary electron efficiency and backscattering efficiency, the conditions needed for this erasing will be explored.

Figure 6.9a demonstrates a two-dimensional study of the efficacy of this dissolution process varying amounts of writing and erasing fluence. Writing was performed at 3 kV, 5 kV, and 7 kV over a range of 0-20 x10^4 μC/cm^2, whereas subsequent erasing was performed at 1kV with varying fluence also ranging from 0-20 x10^4 μC/cm^2. From figure 6.9b-d dissolution of the extracted silver occurs when the initial patterning fluence remains below a threshold. Erasing the 3 kV pattern proved the most effective, with color disappearing up
Figure 6.9: Erasing using a low energy, 1kV beam. a) Crossed gradient pattern varying from 0-20x10⁴ µC/cm², where the second pattern is performed using a 1kV electron beam. b-d) Optical images of erasing test for 3kV, 5kV and 7kV in initial patterning, followed by a second 1kV gradient. For each test, low initial fluences are effectively erased due to the reverse current generated in subsequent low energy patterning.
to fluences of $9 \times 10^4 \, \mu C/cm^2$ when using $20 \times 10^4 \, \mu C/cm^2$ erasing fluence. Similarly, colors from 5kv and 7kV patterning were erased for fluences up to $5.25 \times 10^4 \, \mu C/cm^2$ and $4.8 \times 10^4 \, \mu C/cm^2$ respectively. Some of the variation in apparent erasing effectiveness at different beam voltages is likely due to the reduced electron efficiency of writing at 3kV, which results in less actual fluence compared to primary beam fluence at lower e-beam accelerating voltages.

An interesting observation is that the erasing threshold is not a linear function of initial patterning fluence, as would be expected for a simple reversal of the color generation process. The disappearance of color in the adjacent control portion of the gradient indicates that the dissolution of silver is not entirely localized to the erasing beam pattern. One hypothesis is that charge accumulation from excess erasing fluence induces silver dissolution in nearby areas. In areas where the patterning fluence is above the observed erasing threshold, erasing partially reverses the initial coloring effect resulting in colors equivalent to those found from lower initial fluence. While erasing with higher fluence is more effective at removing color, the higher fluence also results in particle or void formation in the substrate. These defects are a result of patterning at 1 kV, and are visible as well in erased and partially erased initial patterns independent of initial patterning voltage.

Applied erasing of a pattern is demonstrated in Figure 6.10. Figure 6.10a describes the patterns for writing and erasing; the former consists of repeating radial triangular gradients written at 5kV, while the latter consist of two uniform fluence rectangles written at 1kV. In Figure 6.10b the initial pattern is written with a maximum fluence of $6 \times 10^4 \, \mu C/cm^2$, which is near the threshold for erasing. Due to the spreading effect of over-erasing, the entire pattern is removed at both $10 \times 10^4 \, \mu C/cm^2$ and $20 \times 10^4 \, \mu C/cm^2$ erasing fluence since the average writing fluence, $3 \times 10^4 \, \mu C/cm^2$, is well below the threshold of $4.60 \times 10^4 \, \mu C/cm^2$ for $10 \times 10^4 \, \mu C/cm^2$ of erasing. Figure 6.10c demonstrates that for a slightly higher maximum writing fluence of $8 \times 10^4 \, \mu C/cm^2$, erasing at $10 \times 10^4 \, \mu C/cm^2$ is no longer sufficient to completely erase the original rings, while $20 \times 10^4 \, \mu C/cm^2$ is still effective. An alternative mode of erasing is demonstrated in Figure 6.10d, where the writing fluence is chosen to distinctly cross the threshold of erasure. In this case, observance of the erasing threshold results in high contrast between the fully removed low fluence portions and the rings which received a high initial fluence. Aside from the
Figure 6.10: Example of pattern erasure using low voltage e-beam patterning. a) Upper: Bitmap used to generate an initial pattern using a 5kV beam. Lower: Image used to subsequently erase parts of the image by using a 1kV beam. b-c) Upper: Optical images of initial patterning performed at maximum fluences of $6 \times 10^4 \mu$C/cm$^2$ and $8 \times 10^4 \mu$C/cm$^2$ respectively. Lower: Optical images of similar patterns followed by erasing step. d) Optical images for a maximum fluence of $12 \times 10^4 \mu$C/cm$^2$ in the initial pattern and the resulting partial erasure after low voltage secondary patterning. Since portions of the initial pattern exceed the threshold for erasing, only some of the pattern is bleached. Scale bars are 10 microns.
primary erasing effect, surrounding the erasing rectangle pattern are several notable features. Immediately surrounding the erased pattern is an area of over-erasing that is strongly dependent upon erasing fluence which exceeds the minimum needed. This is surrounded by a nearly unaffected region, followed by a double halo. The halos, while not well understood are also similar in size to the halos seen in in Figure 6.9.

6.4 Optimized Erasing

In Figure 6.9 and 6.10 there was clear expansion of the erased area beyond to the intentionally erased areas. In both cases it is possible that the varying writing intensity interfered to extent in the expected erasure of nearby areas. To better optimize erasing conditions, a set of experiments were performed over patches of constant fluence in both writing and erasing. Squares 12 µm in size were patterned ranging from 0.2-1.0 nC/µm² at both 5kV and 7kV. To observe the over erasing effect, smaller 6 µm squares were patterned inside the large colored patches. Erasing was tested at 0.6kV, 1.2kV, and 1.8kV for fluence ranging from 0.2-1.6 nC/µm². Figure 6.11 displays the samples as they appear in bright field reflection. Figure 6.12 displays the same information taken under dark field illumination which would highlight surface scattering. Since the surface is predominantly free of surface roughness this effect is not visible. Instead, the oblique illumination reflects from the silver film behind the glass, providing a view of the pattern in transmission.

For both writing voltages, it is clear that erasing is ineffective for above 0.8 nC/µm², consistent with the earlier analysis. While not clearly visible in reflection, in transmission some erasure can be seen at from 0.6-0.8 nC/µm² for erasing voltages of 0.6kV and 1.2kV and at 0.4 nC/µm² for erasing at 1.8kV. Overall it can be seen that erasing at 1.8kV appears less effective. This is likely due to 1.8kV being closer to the \( E_1 \) voltage, resulting in less total stage current for the given primary beam fluence. At 0.6kV and 1.2kV, over erasure can be clearly seen when attempting to erase 0.2 nC/µm² patterns. Only when using a similarly low erasure fluence of 0.2-0.4 nC/µm² does the erased area match the patterned area. At 0.4 nC/µm² of writing fluence, there is high contrast between the written and erased area, with a clear transition from only partially erased patterns at low erasure fluence to over
Figure 6.11: Parametric study of writing and erasing fluences in reflection. Parts a, c, e are written at 5kV, with the erasing beam varying from 0.6kV to 1.2kV to 1.8kV respectively. Parts b, d, f are written at 7kV, with the erasing beam also varying from 0.6kV to 1.2kV to 1.8kV respectively. Scale bar is 12 μm.
Figure 6.12: Parametric study of writing and erasing fluences in dark field view. The silver back plane supporting the AgIAgPO$_3$ glass (not in focus) reflects light back through the patterned areas additionally providing a view in transmission. Parts a, c, e are written at 5kV, with the erasing beam varying from 0.6kV to 1.2kV to 1.8kV respectively. Parts b, d, f are written at 7kV, with the erasing beam also varying from 0.6kV to 1.2kV to 1.8kV respectively. Note that these images are still full color similar to Figure 6.11. Scale bar is 12 $\mu$m.
erased patterns at 1.6 $nC/\mu m^2$ erasure fluence. One interesting effect is that while the erasing pattern can be seen at high fluence in reflection as a darkened square, in transmission this pattern is not visible despite dark field imaging typically highlighting small particles which act as scattering sites.

So far erasing colors has been demonstrated from solely a single write erase cycle. Figure 6.11 shows that extended erasing in a location from which there is no silver do dissolve results in a slight visible darkening of the patterned area along with the creation of nanoscale features. It is not clear, however, if this effect is caused by a lack of silver to remove, or more general damage to the glass from the electron beam irradiation. To examine whether erasing fully reverses the changes in the glass, three write/erase pairs were chosen from figures 6.11 and 6.12 at 7kV and 1.2kV for writing and erasing respectively, such that the write and erase doses appeared to best match-fully removing color traces without causing over erasure. Pair A involves 0.2 $nC/\mu m^2$ involves writing followed by 0.3 $nC/\mu m^2$ erasing fluence. Pair B is 0.3 $nC/\mu m^2$ writing fluence followed by 0.8 $nC/\mu m^2$ erasing fluence, with pair C consisting of 0.4 $nC/\mu m^2$ writing fluence followed by 1.2 $nC/\mu m^2$ erasing fluence. Figure 6.13a highlights these write erase pairs. Figure 6.13b demonstrates three write/erase cycles in both bright and dark field reflection. As in evidenced by the left pair all three conditions, after the first erasing the color is removed. However, upon a second writing the a different color is achieved, and erasing is only partially effective. Continuation to a third cycle appears even less effective, with neither the colored nor erased portion appearing as in the original cycle. While multiple write/erase cycles were not successful here, it may be due to inadequate matching between the write/erase fluence. Matching the pairs using the actual stage fluence could potentially eliminate the insufficient erasing found on the second erase step. However, the distinct change in color between the first and second write steps may indicate that the erasing process does not fully revert the glass to the initial state. Damage to the glass itself, due to the electron beam may affect repeated extraction of silver, leading to different color states. Moreover, the difference in penetration depth between the write and erase beams, due to their different energies, may lead to inherent layering of beam damage which affects subsequent color formation. At this stage more careful analysis of the dosage and glass structure is needed to determine if repeated stable cycling of color is possible.
6.5 Conclusions

We have investigated a range of process parameters for color production using an electron beam and ioni­cally conducting glass. Irradiated glass compositions of varying ionic conductivity were successful at generating color, as long as AgI was present. The widest range of colors were found in the highest AgI content glasses, due to the high ionic conductivity and increase in refractive index that AgI contributes. Though use of higher energy electrons was explored, at energies above 10 keV little visible surface coloration was observed. Meanwhile, if the energy of electrons in the beam was too low, the large number of secondary electrons ejected from the surface reversed the net current preventing the reduction of silver ions.

In fact, the oxidizing current at low beam energies was sufficient to dissolve the color-generating silver nanoparticles, allowing some colors to be erased. The appearance of a threshold fluence for which color is not removed likely indicates that larger nanoparticles are more stable. Moreover, when applying greater oxidizing current than needed to dissolve color locally, the bleaching became less localized. Overall, the ability to precisely control color in reflection and optical density in transmission as well as erasing portions of the pattern if desired makes this microscale writing process highly flexible.

Testing the robustness of the relationship between electron fluence and resulting surface color found that the overall rate of patterning produces only minor changes in color. However, decomposition of patterning fluence into many passes of shorter duration—to meet hardware limitations—results in large changes to the resulting surface color. For larger scale patterning, generating reliable and robust color generation warrants further exploration, especially if shorter beam dwell times are to be exploited.

This process has potential uses for full color reflective printing such as for security tagging and color filtering applications. Though the glass compositions examined do not pass ultraviolet light, this work shows that coloration of the glass is not limited to a particular composition and therefore further work may make high resolution greyscale photolithographic masks possible. Moreover, the reversible nature of the writing process indicates that there may be additional display applications depending upon the robustness of the glass to write-erase cycles.
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Figure 6.13: Write erase cycles for 3 experimental conditions. a) Three write/erase fluences chosen for writing at 7kV followed by erasing at 1.2kV. b) For conditions A, B, and C, writing ($W_x$) and subsequent erasing ($E_x$) are performed 3 times and optical images are displayed to demonstrate the effectiveness of the write erase process over multiple cycles. Scale bars are 12µm.
In Chapter 5, silver was extracted from AgIAgPO$_3$ glass in small amounts using an electron beam. With this process, it was shown that for low electron fluence, location of the silver could be determined by the electron beam raster path. This is due to the inherent localization of electrons to the vicinity of the impinging electron beam, due to the low conductivity of electrons within the ionic conductor. Increased electron fluence eventually leads to sufficient silver precipitation which form a silver film. At this point, however, electrons become free to move laterally within the metallic film, regardless of the position of the electron beam.

In this chapter, two methods are explored that attempt to control the growth direction of bulk silver extracted from the AgIAgPO$_3$ glass. In the first section, preferentially vertical silver growth is attempted by physically confining the extraction area. If successful, this technique would allow the directed growth of high aspect ratio silver wires, which have applications in water purification.[113, 114, 115, 116, 117, 118] The second section details a process for achieving the reverse goal: preferential lateral growth of silver films. First the typical morphological pattern of silver growth from a microelectrode is demonstrated. Through the use of electron beam surface prepatterning, the lateral spreading of the the silver film can be greatly enhanced, allowing precise lateral extraction of silver films at faster rates than possible with e-beam alone.

7.1 Confined Growth

When a bulk film of silver exists on the surface of ionically conductive AgIAgPO$_3$ glass, further extraction of silver occurs through reduction of silver ions at the glass-metal interface. Those metal atoms are quickly in-
Figure 7.1: a,b) AgIAgPO$_3$ glass pillar patterned with FIB. c,d) Silver extracted on glass surface with electron beam irradiating the central pillar. 

Corporated into the adjacent silver grain causing grain growth. The growth of these grains can be vertical—by displacing the existing grain upward—or lateral. However, the lateral growth of silver grains adds additional contact area with AgIAgPO$_3$. Despite the localized incorporation of silver atoms into adjacent grains, spreading of the silver film from the original pattern is facilitated by the continued contact with AgIAgPO$_3$ at the periphery. Therefore, experiments were conducted in an attempt to limit the interface of the glass with the newly extracted silver.

In an initial attempt at lateral confinement, a focused ion beam was used to mill a pillar of AgIAgPO$_3$. When an electron beam is incident on the top of the pillar, the free space around the pillar prevents the increase in silver-glass contact. The pillar, shown in Figure 7.1a-b, varies in diameter from 1300nm wide at the base to 600nm in diameter near the tip and is 4.9$\mu$m.
Figure 7.2: Tilted view of side wall of milled cavity after irradiating center pillar. Low energy secondary electrons escape from the pillar to land on the side wall, extracting thin filaments of silver.

tall. A 10µm diameter area around the pillar is removed by FIB milling to provide visibility around the pillar. Though exposure to an ion beam does induce a net positive charge to the substrate, the high material removal rate makes the charge-induced effects from ion milling negligible.

Figure 7.1c shows that instead of growing silver at the top of the pillar, initially silver grows out of the pillar base, with additional silver appearing in the perimeter of the milled area. The location of the beam is visible as an indentation in the tip of the pillar. Further electron irradiation, shown in Figure 7.1d, does not cause silver growth on the pillar so much as it causes growth of silver in the surrounding area. It is possible that there is little growth on the pillar itself due to the limited silver ion conductivity and instead simply serves as a target for secondary electron generation.

Figure 7.2 shows a tilted view of the feature after patterning where a large amount of silver is extracted from the side wall of the glass. These particles are small in size, typically consisting of filaments 50nm thick, forming a wiry surface that is physically separated from the central pillar. The appearance of these filaments can be readily explained due to the interaction of the beam with the pillar. Since the width of the pillar is of the same order as the interaction volume, a significant portion of the low energy secondary electrons escape from the side of the pillar. In this case these electrons can then be captured by the nearby glass wall. Due to the extremely low energy of these electrons, they have negligible interaction volume instead causing silver ions
to be reduced directly, generating isolated silver filaments. These filaments then collect and transport further charge to the base of the filament, leading to lengthening of individual filaments. This process differs from irradiation with higher energy electrons in that the silver particles are formed essentially on the glass surface rather than in subsurface particles, allowing the filaments to grow individually as opposed to forming a single conductive film. It is clear from this experiment, that simply laterally confining AgIAgPO$_3$ in the form of a pillar is insufficient to produce laterally confined silver due to the transfer of secondary electrons out of the targeted area.

An alternative method to laterally confine silver growth is to introduce a dielectric layer to prevent charge transfer and physically block growth in undesired directions. To achieve this, AgIAgPO$_3$ was coated in 12nm Al$_2$O$_3$ via ALD. This thickness of alumina is insulating to low energy electrons, but thin enough that 5keV primary beam electrons can penetrate. Once a silver feature is established, further lateral growth by charge transfer at the periphery of the feature is blocked by the alumina. At this point lateral growth would be limited to the directionality of the peripheral grain growth, which would be primarily vertical.

Figure 7.3a depicts the results of placing an electron beam on the glass surface for an extended time. Since there is no method for alumina removal via the electron beam, the area affected by the interaction volume becomes highly damaged, with the Al$_2$O$_3$ remaining on the surface in small particles. However, further away from the beam lateral growth does not appear significantly impeded by the top alumina coating as hypothesized. Instead, the increase in surface area caused by the creation of the silver button has supplied sufficient tension to cause a crazed surface.

Figure 7.3b-d demonstrates a related technique where the surface is first prepared by ion milling a 400nm wide channel to remove the alumina layer, exposing an ionically conducting surface. In Figure 7.3c the electron beam is placed at the end of the channel, whereas in Figure 7.3d the beam is placed in the center. In both cases, locally, there is only limited success in limiting the later growth of silver. However, the exposed glass on the side walls of the channel grow silver at an extended distance from the location of the e-beam. This can be viewed as a partial success in directed silver growth, however a majority of silver extracted is not localized to these regions. Still, from the relatively confined nature of silver growth in this region far from the
Figure 7.3: Silver extraction on AgIAgPO₃ coated with 12nm Al₂O₃. 

a) Electron irradiation at a single location causes silver extraction which fractures the Al₂O₃ film. Direct beam damage to Al₂O₃ visible in the center. b) FIB milling a channel to expose an AgIAgPO₃ surface. c,d) Growth of silver after irradiation at the end (c) and center (d) of the channel. Silver growth preferentially follows along the exposed AgIAgPO₃ surface within the channel, but is not constrained to the exposed surfaces.
Figure 7.4: Silver extraction from AgIAgPO3 covered in 500nm silicon nitride. a) Openings FIB milled through the nitride layer. b,c) Silver extracted openings. d) Optical image showing subsurface growth of silver, rather than extrusion through the prepared nitride opening. Scale bar is 10µm.

interaction volume of the electron beam, 12nm of Al₂O₃ appears to provide some restriction to lateral surface growth since the silver extracted in the channel does not appear to grow onto the coated surface. It is not clear in this instance whether the channel primarily acts to guide secondary electrons in a particular direction, or whether growth occurs by extending the silver-glass interface in a direction not blocked by the insulating layer.

As shown in Figure 7.3, thin insulating layers are not strong enough to remain intact when silver grows underneath. Since a thicker layer may remain strong enough to avoid tensile failure, a sample of AgIAgPO3 was melted against a 500nm thick silicon nitride membrane. A focused ion beam was
then used to provide access to the underlying glass as shown in Figure 7.4a. Given the much stronger nature of this thicker insulator, it was desired to confine the growth of silver both by closing off further increase in silver-glass contact area, as well as providing a physical barrier to silver growth, such that the extracted silver was forced to extrude through the opening in the membrane. Figure 7.4b,c show views of one such opening after application of $400\, nC/\mu m^2$ (1.26nC total). It can clearly be seen that there is silver extracted from both the sides and bottom of the exposed glass. However, there is little extrusion of the silver out of the nitride opening despite the deposition of a large amount of charge. Figure 7.4d clarifies the result in an optical view that provides backside illumination, showing that silver has instead been extracted below the insulating layer. Despite the structural integrity of the insulator remaining intact, the silver does not remain confined.

Since all silver growth in this process occurs at the silver-glass interface, lateral confinement of silver growth using an insulating layer ultimately relies on which process is least energetic: inserting silver grains into the bulk glass, at the interface between the glass and insulator, or by deforming the existing silver to create space for a new interfacial grain. Figure 7.4 appears to indicate that the first two processes require lower energy than the third. It is not clear, however, whether silver is breaking the interface with the glass from that experiment.

Figure 7.5 exposes this nitride-glass interface by milling an additional ring around a central hole leaving an annular portion of silicon nitride with 750nm inner diameter and 1.9$\mu m$ outer diameter. To test the interfacial strength between the insulator and ionic glass, the electron beam is placed in the center of the hole to cause silver to be extracted. Figure 7.5b shows the progress after -105nC and Figure 7.5c-d shows the results after -210nC of charge applied by the beam. As is clearly visible, the nitride ring is elevated by the extracted silver, without providing impediment to lateral growth. Although Figure 7.5d shows that the silver has risen above the height of the insulating layer, the silver appears to also be continuing to grow laterally.

While there may be some conditions in which tall silver wires may be produced by confining lateral growth, the experiments demonstrated here showed that lateral growth is difficult to limit. Nearby exposed glass surfaces are susceptible to the capture of low energy secondary electrons which
Figure 7.5: a) E-beam silver extraction with exposed nitride-glass interface. b) with electron beam only in the center, silver extraction grows laterally breaking the nitride-glass interface, lifting it up. c) Doubling the total current leads to further lateral growth d) Tiled view showing nitride ring completely detached from glass. Height and volume of silver extracted are consistent with silver grown without any confinement.

result in the growth of 50nm silver hairs. Moreover, while insulating layers block charge transfer, the pressure generated by growing silver grains is sufficient to break both the adhesive interface with the insulating layer, as well as the cohesive forces which prevent growth directly into the bulk glass. Further work in this area should be directed towards tailoring grain growth to individual grains rather than films, where oriented crystal growth may dictate the crystal dimensions rather than physical barriers.
7.2 Laterally directed growth of Ag

The high ionic conductivity of AgIAgPO$_3$ means that silver can be extracted and dissolved from the material in a variety of ways. In solid state superionic stamping, the ionic conductor is brought into selective contact with a bulk area of silver film, where silver can be anodically etched in an overall large area of contact which leads to the potential for high throughput. With electron beam irradiation, it was shown that the charge deposited onto the glass was enough to extract silver nanoparticles which at sufficient fluence merge to form a silver film. However, the current of an electron beam is severely limited. Typical beam current for an SEM varies from 20pA-20nA, with beam performance diminishing at high current due to electrostatic repulsion within the beam. For patterning of large areas of silver films on AgIAgPO$_3$ glass, excessively long patterning time can be the primary limitation in silver extraction.

An alternative to using an electron beam to extract silver would be to simply place a conductive electrode on the surface and apply a negative bias. Figure 7.6 demonstrates this process using a tungsten probe. In figure 7.6a the probe is placed on the glass surface. Figure 7.6b-c shows the result of extracting silver by applying a current of -20nA for 300 seconds for a total charge transfer of 6$\mu$C. The resulting silver structure, approximately 15$\mu$m in diameter, shows that at this scale and current density, silver can be extracted at what would otherwise be the maximum current attainable by conventional SEM. In figure 7.6d, this process is taken one step further by applying -500nA for 100s resulting in a total of 50$\mu$C charge transfer. Despite being over eight times the total charge transfer, the area covered by the particle only increases by a factor of 5, indicating that the feature is growing in height as well as width. This places limitations on this technique for extracting large areas of silver, as there is little control over film thickness or shape. Large silver patterns will inevitably end up varying significantly in thickness from the edge to the center of the pattern. Even at this current density, the naturally dendritic tendency of silver growth is also apparent; the pattern shape is roughly circular with branching ridges in all directions.

The limitation of silver extracted from a probe in this way is that the extraction of silver is dependent upon completing the circuit by bringing electrons into contact with the glass surface. Since the large particle provides a
Figure 7.6: Tungsten probe used to extract silver from AgIAgPO$_3$ glass.  
a) Probe making contact with the glass.  
b) Application of -20nA for 300s for a total of 6$\mu$C charge transfer.  
c) Silver particle remaining after probe is removed.  
d) -500nA applied for 100s for a total of 50$\mu$C.  The particle grows in thickness and laterally as charge is supplied, forming a roughly circular shape.
large silver-glass interface, silver extraction is primarily directed underneath the existing particle, increasing its height while only slightly increasing the lateral dimensions. At high overall current densities, the local silver ion concentration underneath the particle begins to appreciably decrease. The increased relative silver ion concentration near the perimeter of the particle allows silver to preferentially deposit along the edge. This growth is unstable, however, since the extension of the particle edge increases the distance from the silver ion depleted region. This causes further preferential extraction along the perimeter and ultimately dendritic growth. Ultimately, in this scenario the lateral growth of silver around an electrode is limited and uncontrollable due to a limited mechanism for controlled lateral spreading.

For probe-based growth, the controlled extraction of silver relies on slight variation of silver ion concentration to provide lateral growth. However, lateral growth could occur more rapidly, if the electrical charge supplied by the probe was able to conduct laterally across the surface. A benefit of using an electron beam as an electrode is that it can be incident upon a surface even if that surface is not initially conducting. From previous work, it was shown that even at low fluence, an electron beam can reduce silver resulting in isolated subsurface silver particles. While use of the electron beam to make fully conductive silver films may require high fluence, the presence of silver in an area patterned at low fluence offers the opportunity to increase the electrical conductivity of the surface, and thus the lateral growth when a current is applied by metal probe.

Figure 7.7 demonstrates the effect of so called pre-patterning of the AgIAgPO3 glass surface using an electron beam before placing a probe on the pattern and applying -133nA for a total of 4.2µC of additional charge. In this experiment, a 5keV beam was restored across a 20µm by 20µm square at different amounts of fluence. The squares received 0.66nC/µm², 0.99nC/µm², 1.32nC/µm², and 2.63nC/µm² for parts a-d respectively. As is evident in Figure 7.7a-b, the effect of the e-beam patterning is to provide some directional preference to the growing silver particle. The rate of lateral growth is increased in the patterned area relative to the pattern-free area. Figures 7.7c-d demonstrate that with sufficient prepatterning fluence, the lateral growth rate is sufficient to fully fill the patterned rectangle. Whereas the fluence in Figure 7.7c is marginally sufficient to confine growth to the prepatterned area, the progressive growth of silver in Figure 7.7d was selective enough
Figure 7.7: Effect of pre-patterning with an electron beam upon directed extraction. Each 20µm square is prepared by patterning with a different amount of fluence at 5keV. The probe is then brought into contact with the square and an additional 4.2µC or an average of 10.5nC/µm² fluence is applied. a) 0.66nC/µm² prepatternning, b) 0.99nC/µm² prepatternning, c) 1.32nC/µm² prepatternning, and d) 2.63nC/µm² prepatternning. Applied at -133nA.
Figure 7.8: SEM demonstrating the propagation of silver to fill the rectangle defined by electron beam. a) Progress of silver film after 2s at -133nA. While silver on the edge of the e-beam defined pattern slowly grows laterally, progression of the silver extraction within the patterned area occurs through the growth of many silver grains leading to a porous, but electrically conductive film. b) Film after an additional 4s at -133nA. Continued electrodeposition fills in the gaps, producing a continuous silver film.

to maintain the original pattern in the final silver film. Further growth of this pattern follows the expected pattern; thickening of the film along with growth around the perimeter increasing the lateral size of the film. While the original pattern is retained initially, further growth reverts to preferentially depositing away from the rest of the film, resulting in increased growth at corners that eventually become dendritic.

While patterning of silver films using an e-beam only typically requires $4-6nC/\mu m^2$ from a $5keV$ beam to fully form a film, prepatterning requires less than half the e-beam fluence to become effective. Figure 7.8 shows SEM images of the silver on the glass as it spreads across the surface pre-patterned with $1.32nC/\mu m^2$. Clear from Figure 7.8a is that unlike lateral growth in unpatterned areas, the growth in the patterned region first forms a percolation network of silver particles. Since isolated silver particles exist in the patterned region prior the application of current through the probe, all that is required for propagation of the electrode is for the particles to increase in size until they make electrical contact with their neighbors. This allows quick spreading of electrical conductivity to the entire patterned region, which can then be followed up with extraction of silver across the entire electrode to
fill in the voids. This also explains why the fluence needed for this effect to be noticeable is a significant fraction of the fluence needed to produce a film with e-beam alone. At low fluence below $1nC/\mu m^2$, embedded silver particles are a small volume fraction and thus cannot easily form an electron percolation network.

Pre patterning with an electron beam offers a way to make larger silver films with less total e-beam patterning time, but the propagation speed of the percolation network needs to be considered to ensure that the entire pattern is filled with little unwanted growth in the surrounding unpatterned areas. To assess the propagation speed of the percolation network—as a function of the charge applied and the patterned perimeter length to unpatterned perimeter—an experiment was conducted with results shown in Figure 7.9. The pattern consists of a $20\mu m$ by $20\mu m$ square, with a $5\mu m$ line extending from one side. The purpose of the square is to establish a well-defined area of silver such that the change in area as the silver film propagates along the line is kept minimal. Figure 7.9a-b depicts application of an additional -212nC by probe to an area prepatterned with $1.32nC/\mu m^2$ by electron beam, where the overall change in silver area along with the distance change along the line were recorded. The same procedure was applied to the pattern in figure 7.9c-d where the initial fluence was $2.63nC/\mu m^2$.

For both patterns, it is interesting to note the high selectivity with which the additional area covered by silver favors the patterned area. By comparing the total increase in area—including the increase in dimensions of the left square—to the nominal increase in area seen in the progression of silver along the line, it is found that 64% and 80% of the added silver area lie within the patterned line for $1.32nC/\mu m^2$ and $2.63nC/\mu m^2$ respectively. By correcting for the larger perimeter of the square relative to the propagating front, it is found that the lateral growth rate in the patterned region is 38 and 80 times that in the unpatterned region.

While the pattern above is relatively simple, the high selectivity for lateral growth in patterned regions allows for complex patterns with long path lengths. Figure 7.10 demonstrates some of these complex patterns. Figure 7.10a-b consists of an initial attempt to pattern using two intersecting $50\mu m$ squares. The prepatterning consisted of $-1.1\mu C$ of primary beam charge deposited at $5keV$ in single pixel wide lines. Due to the ill-defined width of the pattern (likely 100-300nm) the prepatterning fluence was likely 9-28$nC/\mu m^2$. 
Figure 7.9: Characterizing propagation selectivity of patterned to unpatterned area for 1.32\(nC/\mu m^2\) (a-b) and 2.63\(nC/\mu m^2\) (c-d). Line in b) and d) indicates the silver growth distance in the patterned area for an additional 212nC charge transfer over the images in a) and c) respectively. Comparing the propagation velocity in the e-beam patterned area to unpatterned area, parts c, and d grew 38 and 80 times as fast, respectively, as the rest of the lateral growth into unpatterned areas.
An additional -20µC was applied via a probe at one corner of the pattern at a current of -2.5µA. The large charge transferred to the substrate in this example easily forms a conductive pathway along the squares. The additional charge was then directed towards extracting silver perpendicular to the lines with a clear grain growth direction. Also visible in the image is a slight narrowing of the lines as they progress away from the probe. Moreover, the high fluence of the initial line appears to have inhibited silver growth directly on the pattern, favoring instead to develop on either side of it. This is likely due to damage in the glass in the path of the beam, with the pattern being sufficiently narrow to accommodate the resulting silver extraction to either side of the damaged glass.

Figure 7.10c-d depicts a more controlled complex pattern of inscribed rings patterned with an initial fluence of 3.95nC/µm². The rings, given a finite width of 0.7-1µm spread the beam influence such that a continuous line is formed. A total of -2.95µC was applied to the probe for a nominal fluence of 12nC/µm² for the original pattern. As can be seen in this pattern as well, there is a slight widening of the features closest to the probe, which were the first to form. However, the lower current of -300nA results in better definition along the pattern boundaries when compared against the interlocked square pattern.

All of these experiments in probe based silver extraction were carried out at controlled current chronopotentiometry. It was found particularly interesting that the voltage required for extraction remained nearly constant at -250mV to -80mV for a large range of extraction current once a silver film had formed. To investigate the I-V characteristics of this process, a series of 20µm Ag squares were created with probe current ranging from 5nA to 5µA as shown in Figure 7.11a. All the squares were prepatterned with 1.32nC/µm² fluence from a 5keV beam and received an additional -3.9µC (nominally 9.75nC/µm²) via probe. Two of the squares (1µA and 5µA) were repeated due to electrical noise during extraction, but the rest provided stable voltages in the second half of the silver extraction, where a film was fully developed.

\[ j = j_0 \left[ e^{-\alpha f(E-E_{eq})} - e^{(1-\alpha)f(E-E_{eq})} \right] \]  

(7.1)

Figure 7.11b plots the current density vs voltage relationship in a Tafel
Figure 7.10: Complex shapes generated through pre-patternning at 5keV. 
a) Interlocking square pattern with a primary beam charge deposition of -1.1\(\mu C\). b) SEM of silver extracted after -20\(\mu C\) applied via tungsten probe. c) Linked ring pattern irradiated with 3.95\(nC/\mu m^2\). d) Linked rings after an additional -2.95\(\mu C\) applied via probe.
Figure 7.11: a) SEM of 20µm squares applied at current ranging from -5nA to -5µA. b) Tafel plot of the current density from a), along with the Butler-Volmer equation fitted to the data.
Figure 7.12: Initial results of silver removal for reversed voltage. a) A large particle of silver grown without e-beam patterning. b) Results after applying a reverse bias (150mV) to remove the extracted silver. Disappearance of the highlighting caused by the lower detector in the second image shows that the thickness of the feature has decreased significantly.

The data are found to follow the Butler-Volmer equation (equation 7.1). In this equation, $E_{eq}$ is the equilibrium voltage, $j_0$ is the exchange current, and $\alpha$ is the charge transfer coefficient. Though there are a number of heuristics to analyze Tafel plots and extract these parameters, instead a nonlinear least squares fit was performed to fit to the Butler-Volmer equation directly, with data points weighted logarithmically to reflect that the precision of the potentiostat varies with different current ranges. The $E_{eq}$, where current begins to flow, was fit to -87mV and matches well in magnitude with experimental results for etching silver in S4.[56] This low activation voltage reflects the low energy need to drive silver in AgIAgPO$_3$, giving the glass its high ionic conductivity. The exchange current was fit to be $j_0 = 0.00016A/cm^2$. Of interest in this analysis was that the charge transfer coefficient in this model was found to be approximately 1, instead of a more conventional value near 0.5. This indicates that the oxidizing and reducing pathways for silver in the patterned area are very different, though the exact reason behind this is unknown. Since the magnitude of the voltage was found to be decreasing over time, it is not likely that the system was experiencing mass transport limitations.

Future work in this area is needed to determine how the electron beam may be affecting the system as well as if the reverse process (silver dissolu-
tion on microelectrodes) does indeed follow a different pathway. Figure 7.12 demonstrates that silver dissolution is possible with reversed bias. In figure 7.12a, a large silver pad is grown on the glass, with the SEM highlighting the three dimensional nature of the feature. With reverse bias (shown in Figure 7.12b) the structure effectively deflates as silver is removed. Instead of a reverse process where the feature dissolved into the glass perimeter first, there is a porous matrix left behind.

7.3 Conclusions

Overall, it has been shown that it is much easier to increase lateral growth rates rather than to inhibit them. The addition of embedded silver provided by electron beam charge transfer in a pre-patterning step, effectively allows the controlled growth of silver films on an ionically conducting glass AgI\textsubscript{3}AgPO\textsubscript{3}. Growth of the silver film occurs by growth of the peripheral silver grains which then make electrical contact with nearby embedded silver particles to create an electronically conductive percolation network. Growth of this conductive network propagates laterally up to 80 times the regular lateral silver growth for the conditions tested. The high selectivity for lateral silver growth of the electrode within the prepatterned area results in the electrode quickly filling the prepatterned area, and allowing generation of a silver film that takes on the prepatterned shape. Because of this, complicated film geometries can be generated for which path length of the metal is much longer than distance to the current supplying probe.

Electrochemically, this process appears facile, requiring low voltage and displaying little mass transport limitation or ohmic resistivity due to ionic conduction. The supplied current can be several microamperes, much higher than that found from traditional electron beams. Moreover the high selectivity is seen at probe current densities as high as 0.125 $A/cm^2$, while at higher current densities dendritic spreading of the silver film begins to be observed. Furthermore initial examination of reverse voltage shows that the silver can be oxidized back into ionic form within the glass, though it leaves behind a porous matrix in its place. Further work could extend this process characterization to optimize the electron beam parameters to minimize the total fluence needed as well as maximize the selectivity for growth within the
patterned area. Additionally, further electrochemical characterization may extend the range of effective current densities for writing as well as better characterize the silver dissolution regime in reverse voltage. The versatility of this process shows promise for optical systems where a complexly shaped reflector is desired, or where it is desired to generate small silver structures such as in plasmonic sensing.
CHAPTER 8
CONCLUSIONS AND FUTURE WORK

In summary, this work developed several processes for silver patterning centered on the use of AgIAgPO$_3$ glass electrolyte for both the large area etching of silver films, and direct write extraction of silver on AgIAgPO$_3$ surfaces.

Although there are a number of ionic conductors for silver, AgIAgPO$_3$ possesses several properties that make it a good choice for engineering applications around a solid ionic conductor. First, it has one of the highest room temperature ionic conductivities, meaning that applications can reach significant ionic current without requiring heating. Second, the thermal properties of these metaphosphate glasses are also favorable; the extremely low $T_g$ permits low temperature processing and the stable glass forming region allows the material to be easily molded without concern over electrolyte crystallization or phase separation. Moreover, compared to silver ion conductors of the RbAg$_4$I$_5$ family, materials based on silver metaphosphate are significantly more resistant to degradation by water.

8.1 Synthesis and Fining of $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$

Despite a large body of literature analyzing AgPO$_3$-based glasses which span several decades, only recently has there been emphasis on how sensitive the glass is to the method of synthesis. The exposure to even low levels of moisture is known to dramatically reduce the glass transition temperature—a fact taken advantage of to facilitate low temperature imprinting. In this work, contamination of AgIAgPO$_3$ glass with particulates was discovered to be due to the use of alumina crucibles which were used to avoid needing costly platinum crucibles. Through successful identification of the particulates, a fining step was demonstrated which reliably removes larger particles in $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ for $x \geq 25\%$. Moreover, synthesis using nickel crucibles
appears promising as a method for eliminating the source of the contamination. This should prove useful for both improving optical overlay in S4 as well as other demonstrated optical applications where the elimination of scattering sites is important.[49, 119, 50, 52, 53]

8.2 Implementation of AgIAgPO$_3$ in S4

Substitution of Ag$_2$S in the S4 process for AgIAgPO$_3$ was demonstrated to result in all-around improvement in the patterning of silver films with the S4 process. In terms of ultimate patterning resolution, AgIAgPO$_3$ successfully patterned 30nm features, comparable what was possible with Ag$_2$S and primarily limited by the resolution of mold features that were available at sub-100nm length scales. Reliability of AgIAgPO$_3$ stamp patterning in S4 was also increased over that of Ag$_2$S stamps. Whereas Ag$_2$S is polycrystalline and contains grain boundaries which erode with use, the amorphous AgIAgPO$_3$ glass possesses no grain boundaries to erode. Moreover since Ag$_2$S stamps are mixed conductors, during stamping there is significant electronic conduction which is a detriment to S4 in two ways: first, the electronic current contributes to the overall measured current, and second the mobile electrons within Ag$_2$S can combine with Ag$^+$ ions to deposit silver metal within the electrolyte. AgIAgPO$_3$ solves both these issues by being solely an Ag$^+$ ion conductor.

While the material properties of an AgIAgPO$_3$-based S4 stamp improve the many aspects of the S4 process, the central factor in improving the overall process is the simplification and standardization of stamp fabrication and patterning, while allowing for future increases in stamp diameter. The original generation of S4 relied on direct patterning of the stamp through FIB milling. While focused ion beam machines are very flexible for patterning, their slow milling speed and small patterning area prohibit their use in economical generation of large stamps. A second generation technique using hard molds to imprint Ag$_2$S stamps permits the fast patterning of large area stamps. However, direct resistless imprinting requires high pressures and pristine, flat surfaces. Such surfaces are typically only seen after great effort on bulk materials or from thin film deposition techniques. While some methods exist for thin film Ag$_2$S deposition, their application to S4 is ill-suited;
thin film stamps are prone to electrical shorting from the deposition of metal on the counter electrode during etching.[120]

Transitioning to a thermally imprinted AgIAgPO$_3$ stamp borrowed from the benefits of direct Ag$_2$S imprinting while removing many of the challenges. To begin with, generation of a contamination free AgIAgPO$_3$ surfaces is trivial since cleaving can produce clean surfaces and simple heating can reform the shape of the stamp to a known configuration. Due to the large pressure needed for patterning Ag$_2$S stamps, ‘blank’ stamps prior to imprinting needed to be almost ideally flat. By way of contrast, AgIAgPO$_3$ stamps begin with a curved surface with single initial contact point. However, since the glass is liquid during imprinting, the stamp can easily be flattened even though much lower pressure is used than with Ag$_2$S imprinting. Moreover, issues of elastic spring-back common in imprinting of a solid such as Ag$_2$S are eliminated when performing thermal nanoimprint.

One drawback to implementation of thermal nanoimprint for S4 stamp patterning is that tighter control and characterization is needed of the processing parameters to achieve repeatable imprinting times and stamp flatness. Towards this goal, dual temperature and force feedback control were implemented on the nanoimprint and S4 system, allowing precise tuning of processing parameters. Characterization of these parameters demonstrated that while the mold temperature primarily determines the imprinting time, increasing the temperature of the stamp holder can cause a transition in overall stamp surface curvature from concave to convex. Thus by varying these two temperatures, a stamp can be imprinted to the desired diameter in a prescribed time, while minimizing overall curvature. Modeling of the contact between one of these nearly-flat stamps and a flat substrate gives realistic estimates of the load needed to make complete surface contact during S4 etching.

8.3 Silver extraction from AgIAgPO$_3$ with an electron beam

By inverting the current and geometry of S4, nanoscale extraction of silver on a solid ionic conductor was demonstrated using an electron beam. Electrons injected by the beam reduce silver to create subsurface silver par-
ticles. Remarkably, for a low fluence this results in a surface which reflects light in vivid colors, but is opaque in transmission. This is attributed to the nanoparticles altering the effective refractive index of the glass near the surface, causing interference film coloration. The opaqueness in transmission is assumed to be due to an increase in absorption caused by the metal particles. For low fluence, the coloration could be reversed by using a lower beam energy which effectively reverses the current transferred to the substrate by the beam. However colors produced at a larger fluence resisted erasing, suggesting that sufficient irreversible structural changes accrued with continued silver extraction. At even higher fluence, a reflective metallic silver film developed. Since prior to the particles becoming a continuous film the surface remains electrically insulating, the electron beam can locally seed the surface with silver particles in an arbitrary pattern. Continued irradiation with the electron beam past film formation fluence results in thickening and lateral growth of the pattern, with no further capability to direct the location of extracted silver; the silver film acts as a simple electrode on the surface.

Additional experiments were performed to try to control the growth direction of bulk silver extracted from AgIAgPO$_3$. Attempts at confining the growth laterally—to force silver to grow vertically—were unsuccessful. However, it was found that partial seeding of the surface by the electron beam with a pre-pattern of sub-surface silver particles greatly enhanced the lateral growth velocity of silver compared to un-patterned regions. A metal probe, capable of carrying several orders of magnitude larger current than the electron beam could then be used to supply the charge needed to connect the pre-patterned area. This technique drastically reduces the time needed to pattern large areas, and results in less damage to the glass from high energy electrons.

8.4 Future work

S4 has demonstrated remarkable patterning resolution at the nanoscale. Future avenues of research can improve this process from different perspectives. Where the S4 already performs well, at the nanoscale, process improvement should involve characterization of solid electrolyte surface degradation routes. In the case of Ag$_2$S stamps, large overvoltage results in the erosion
of grain boundaries. While less pronounced in a homogeneous glass such as AgIAgPO₃, it is likely that some similar degradation occurs with overvoltage. Characterization of this relationship should improve overall stamp lifetime.

Secondly, environmental moisture also causes surface degradation. In the current AgIAgPO₃ electrolyte, the metaphosphate glass former can be slowly hydrolytically attacked, leaving behind porous AgI and silver dihydrogen phosphates. Fortunately, the amorphous structure of silver metaphosphate matrix can small accommodate small amounts various other cations (network modifiers) and network formers without crystalizing or phase segregation. Including one or several of these additions are likely to reduce hydrolytic attack by increasing the overall network connectivity. In linear chains or rings of phosphates, monovalent cations such as silver form weak ionic bonds to a single oxygen on the phosphate. Substitution of the monovalent silver ion with a divalent or trivalent ion results in a weak cross-linking of the phosphate chains since the cation becomes bonded to multiple oxygen atoms. Alternately, a portion of the phosphate network former could be substituted with a network former less susceptible to hydrolysis. Since there are many network modifiers as well as network formers, an extensive literature survey is needed to identify likely stable resistant glasses that retain the beneficial properties of AgIAgPO₃. One common thread to increasing the network conductivity of the glass is the corresponding increase in glass transition temperature, so any additions to the glass composition will likely remain small to keep the glass transition temperature low.

An alternate avenue of research that would benefit S4 is the continued engineering of stamps for large area patterning. When using step and repeat with small stamps, the quantity of silver etched by a single stamp becomes significant, to the point that care must be paid to where the etched silver deposits on the rear of the stamp, to avoid electrical shorting. Alternatively, development of stamps greater than 10mm in diameter will need to consider the location of the back electrode and how to maintain a constant resistance for both the edge and center of the stamp to the back electrode. These issues, as well as the nanoimprint quality for large stamps, will ultimately need to be addressed to make S4 a reliable process for commercial scale nanoscale patterning of silver.

Future work for electron beam metal extraction is to extend this process to other metals, including the corresponding copper equivalent ionically con-
ductive glass. Moreover, at this point the metal films extracted on the glass surface remain attached to the glass. Although the glass is transparent, many potential applications of such a direct write process would prefer the metal be on a different substrate. Therefore, research into transferring these films to another substrate should be pursued.

Solid electrolytes provide an exciting opportunity to extract or etch metals precisely where desired. In solid state superionic stamping, these materials allow nanoscale patterning well below the diffraction limit seen in optical systems, while needing only simple machinery to perform. The long term benefits of perfecting large scale patterning with their use will be to greatly reduce the cost associated with these types of substrates. Direct extraction of metal at the nanoscale can be applied in multiple ways. If this process is scaled up to large areas, materials could be made which can be colored or made reflective on demand, or generate high surface area silver electrodes for water purification. Alternatively, research into plasmonics can benefit from the flexibility of this process, which allows the generation of arbitrarily shaped silver films on demand.
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APPENDIX A

NOTE ON ELECTRON EFFICIENCY FOR E-BEAM IRRADIATION

Monitoring of charge transfer during the e-beam writing process is made challenging by the generation of secondary electrons that are lost from the surface as shown in Figure 5.1. Most measurements of applied fluence are conducted by measurement of primary beam current via a faraday cup. This method is simple to apply since the electron beam current is relatively stable and not affected by substrate composition. Simple integration of the constant beam current leads to a known charge application over a known area.

In most cases, measurement of the stage current during the writing process is much more challenging. Due to the beam rastoring process, the variation in dwell time used to achieve locations with different fluence result in a rapidly varying stage current signal. To accurately calculate fluence requires the synchronization of the beam position information with the current data. In cases where the beam dwell time is kept constant over the entire pattern, however, an accurate measurement of the stage current can be made and correlated with the corresponding fluence.

Figure A.1 shows 10-30\(\mu m\) diameter disks patterned at 5kV and 7kV, with primary beam currents of 6.18nA and 7.15nA respectively measured prior to the experiment. Patterning time was fixed at 25 minutes to allow recording of the stage current, with the disk diameter set to maintain a total primary beam fluence of 4\(nC/\mu m^2\), 10\(nC/\mu m^2\) or 20\(nC/\mu m^2\). The stage current was then measured as the patterning progressed. Figure A.2a shows a plot of the stage current. It is clear that there is a difference in patterning efficiency as silver accumulates in the substrate.
Figure A.1: SEM images of large disks sized to known fluence after 25 minutes of patterning. This allows correlation of the stage current traces with the percent completion of the patterning. a,c) Patterned at 5kV. b,d) patterned at 7kV.
For low fluence (less than $3nC/\mu m^2$ when patterning at 5kV and less than $5nC/\mu m^2$ when patterning at 7kV) the charge collection efficiency is high. The monotonic increase of collection efficiency at low fluence is associated with the extraction of silver particles within the surface. Silver extraction at 5kV patterning occurs closer to the surface, causing a larger change in the beam interaction volume composition than when patterning at 7kV. The transition to lower collection efficiency coincides with the transition to a metallic film of silver on the surface, with an eventual leveling out of the efficiency at high beam fluence. For thick extracted silver films, the beam interaction volume lies completely within the silver layer, resulting in a total emission yield similar to that of bulk silver.

While the measurement of stage current during patterning is more challenging than using the primary beam current, it provides direct insitu feedback for the progression of silver extraction. Assuming the silver retains a bulk density of 10.5g/mL and the process is electrochemically reducing silver, the current can be integrated to calculate the thickness of silver extracted. Figure A.2b demonstrates this conversion to an estimated thickness and plots it alongside other experimentally measured thickness data. Of note is that while the extraction rate based on the primary beam current appears to vary with total primary beam fluence, the direct measurement of stage current accounts for these changes inherently. Moreover, the adherence of the estimated thickness to the measured thickness indicates that process is truly electrochemical in nature.
Figure A.2: a) Plot of the stage current normalized to the primary beam current as a function of primary beam fluence. b) Lines are of the estimated thickness of the disk patterns, resulting from integrating the stage current and assuming the the silver takes on a bulk density of 10.5g/mL. Data plotted is for reference and based on AFM thickness measurements of many smaller patterns. Highlighted region is where colors are observed.