Nanostructure Fabrication by Electron and Ion Beam Patterning of Nanoparticles

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Abstract

Two modes of energetic beam-mediated fabrication have been investigated, namely focused ion beam (FIB) direct-writing of nanoparticles, and a technique for electrostatically patterning ionized inorganic nanoparticles, termed nanoxerography.

A FIB has been used to directly pattern thin films of organometallic Ag-precursors down to a resolution of 100 nm. The sensitivity of the resist to 30 keV Ga⁺ ions was measured to be approximately 5 μC/cm². Using this technique arbitrary structures were fabricated in two and three dimensions with resistivity on the order of 1x10⁻⁴ Ω-cm and 1x10⁻⁵ Ω-cm for single- and multi-layer structures, respectively. A new unit of merit for characterizing direct-write processes, termed resistivity-dose (μΩ-μC/cm), has been introduced.

A Nanocluster Source capable of generating a beam of charged, inorganic nanoparticles has been characterized. The relationship between power supplied to the magnetron of the source and the size of deposited clusters has been plotted. Techniques for utilizing such clusters to develop latent electrified images patterned by an electron beam (EB) have been proposed. The charge-storing characteristics of a variety of substrates such as mylar and polyimide were studied by developing EB-patterned charge images with toner particles.

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1 Introduction

Figure 1: Carbon micro-wineglass fabricated by Matsui et al. utilizing focused ion beam chemical vapor deposition.

This thesis will discuss new processing routes for fabricating arbitrary structures and devices utilizing energy delivered by energetic electron and ion beams. While energetic particles have been used for decades in various lithographic modes, the majority of existing techniques rely on multiple processing stages requiring lift-off, evaporation and etching steps that are both environmentally and economically costly. However, techniques developed in the past twenty years have utilized energetic beams to directly pattern inorganic precursors, primarily from the gas and liquid phase, thus eliminating wasteful evaporation and lift-off steps. Such processes have successfully produced complicated structures with sub-micron features without requiring masks or the high temperatures typically used in silicon processing. The inorganic precursors used in these direct-write techniques typically involve a metal atom or cluster of atoms stabilized by an organic ligand. Available in both gaseous and liquid phases, these inorganic materials have been patterned by a variety of methods. In this chapter, two techniques for patterning such materials will be briefly discussed: beam-induced chemical vapor deposition (CVD) of organometallic gases and the direct-writing of liquid nanoparticle films.

1.1 Beam-induced chemical vapor deposition

One successful approach for in-situ nanostructure fabrication involves beam-induced deposition of chemical vapor precursors. The building block for this fabrication scheme is a gas-phase metal atom attached to an organic stabilizing group. Typically, this
organometallic precursor gas adsorbs onto a substrate and is decomposed by energy delivered from focused beams of electrons, photons, or ions, leaving metal deposits. This technique facilitates the fabrication of nanometer- to micrometer-size structures in one step, thus eliminating subsequent developing, etching, or lift-off steps. The fabrication of complex three-dimensional structures, including unsupported structures, is also possible utilizing beam-induced CVD. While more difficult for electron beam CVD, because of the large penetration range of electrons, focused ion beam (FIB) CVD has been shown to be an effective technique for building such structures. As shown in Figure 2, a pillar can be grown by fixing a beam at position 1, while moving the beam within one pillar diameter a terrace can be formed at position 2, and so on. Using a 30 keV Ga+ FIB, Matsui et al. fabricated a variety of three-dimensional microstructures including coils, drills, and bellows with feature sizes as small as 80 nm. A scanning electron microscope (SEM) image of one such coil is shown in Figure 3.

Although successful in creating high-resolution three-dimensional structures, beam-induced CVD suffers from significant contamination by the organic components of the precursor gas. Hydrocarbon and oxygen contamination from organometallic precursor gases can exceed 50%, thus altering device conductivities to levels unacceptable for many desired applications. Device fabrication by beam-induced CVD is also constrained by a small number of available precursor gases, thus limiting the variety of materials that can be deposited. Finally, because beam-induced CVD is a serial process, deposition...
speeds are very slow as compared to other parallel processes utilizing masks, although progress has been made in the area of multiple beam fabrication. Although these problems have stifled the use of such processes for general fabrication, beam-induced CVD, particularly FIB CVD, is a technique successfully used in the chip and mask repair industry. Many commercially available FIBs are fitted with injector needles and material sources to facilitate in-situ patterning of organometallic gases.

1.2 Patterning nanoparticle thin films

Liquid films of nanoparticles have been patterned to construct a range of active devices and structures by printing\(^7\), embossing\(^6\), and ink-jetting\(^9\) in addition to beam-mediated direct-writing\(^10\). For the most part, thin films of nanoparticles are formed either by spin-coating, sedimentation, or by simply dipping a substrate into a solution of particles. These nanoparticles are typically 2-10 nm in size, and are capped with some type of organic ligand to maintain their solubility and prevent agglomeration. Similar to organometallic gases, thin films of nanoparticles can be exposed with photons, electrons, or in the case of this work, ions. Irradiated regions become insoluble, so subsequent washing in a suitable solvent dissolves any unexposed particles leaving the inorganic pattern in one exposure and wash step. All patterning techniques, beam-mediated or otherwise, require an anneal step to cure the nanoparticles, thus forming a conductive material. Figure 4 shows an unwashed contact pad and line patterned in a film of Ag nanoparticles by a 1064 IR diode laser\(^10\). Figure 5 shows a SEM image of nanoparticles exposed by an electron beam\(^11\).

![Figure 4: Optical image of an unwashed contact pad and line patterned by an IR diode laser in silver. From Griffith\(^10\).](image1)

![Figure 5: SEM image of nanoparticles patterned by an electron beam. From Griffith\(^11\).](image2)
Again, as with beam-induced CVD, the organic components present in these films adversely affect conductivity. The lowest resistivities measured are approximately one order of magnitude greater than that of the bulk material.

1.3 This work

While directly patterning inorganic precursors with energetic beams can readily achieve sub-micron resolutions, particularly when utilizing electron and ion beams, all of the discussed methods suffer in the areas of purity and throughput. These direct-write processes are slow, in part because they are serial, but also because the inorganic building blocks utilized require larger energies for exposure as compared to conventional organic polymer-based resists. Purity will always be somewhat of an issue as long as any organic capping is required for stabilization. The work presented in this thesis seeks to address these issues by investigating two modes of fabrication: FIB direct-writing of nanoparticle films, and nanoxerography, a novel patterning technique based on electrophotography. Directly patterning nanoparticle films with a FIB dramatically increases throughput as compared to electron beam direct-write methods because of the increased sensitivity of resists to ions over electrons. The resistivity of structures fabricated by this method are comparable to other electron beam direct-write processes, and are approximately 3 orders of magnitude lower than prior work in the area of FIB direct-writing of nanoparticle films\(^{12}\). Nanoxerography relies upon ionized, uncapped inorganic nanoparticles to develop charge patterns stored in charge-retaining materials known as electrets. Such nanoparticles, because they are free of any organic ligand, should be theoretically 100% pure. Also, the patterning of electrets with electrons or ions should be rapid, leading to a potentially high throughput process capable of fabricating structures and devices at or very near bulk conductivities.

In chapter two, the inorganic nanoparticle building blocks used in this work are discussed in greater detail. Chapter three reports the patterning of nanoparticle resists by FIB direct-writing. Chapter four presents progress made in nanoxerography, the technique used to electrostatically pattern uncapped, inorganic nanoparticles. Finally, chapter five offers some conclusions and proposals for future work.
2 Nanoparticle Building Blocks

Figure 6: Transmission electron microscope image of a CdSe nanoparticle by Malik et al.\textsuperscript{13}

The patterning techniques reported in this thesis rely on two different types of nanoparticle material sets: organically capped dispersions of nanoparticles in solution, and uncapped nanoparticles suspended in a carrier gas. While the synthesis of solution-based nanoparticles is discussed at length elsewhere\textsuperscript{14}, this chapter will explore the use of a magnetron-sputtering tool for the generation of uncapped, inorganic nanoparticles. Such nanoparticles are an attractive alternative to their liquid-based counterparts because they do not require a stabilizing organic ligand. The general properties of nanoparticles that facilitate their use for beam-mediated fabrication, particularly depressed melting temperature, will also be discussed.

2.1 Depressed melting temperature

The key property that enables the use of nanoparticles in many patterning techniques is their depressed melting temperature. The melting temperature of small particles is close to inversely proportional to the radius, thus leading to a sharp decrease in melting point for particles below approximately 5 nm (Figure 7) in diameter. This behavior has been observed in metal\textsuperscript{15} and semiconductor nanoparticles, most notably silicon\textsuperscript{16}, although exceptions have been found\textsuperscript{17,18}. Of great relevance to this work is the indication that small particles exhibit depressed melting regardless of the type of material\textsuperscript{19}. Thus, fabrication schemes relying on this phenomenon could access a wide material library assuming the availability of nanoparticles in a stable, easily deliverable form. Solution-based nanoparticle systems are attractive because of their convenient transport and ease of deposition. If capped with ligand stabilizers, nanoparticles can be dissolved in a
suitable solvent, thus allowing their delivery to substrates by a variety of methods such as solution-casting, dip-coating, or spin-coating, the method used in this work.

![Graph showing melting point dependence of gold particles as a function of size.](image)

**Figure 7:** The melting point dependence of gold particles as a function of size, as reported in the 1976 work of Buffat and Borel[^5].

Once deposited, liquid nanoparticle films may be converted solid by heating at temperatures around 300 °C, as is the case for Au and CdSe particles with diameters of approximately 2.5 nm. The ideal conversion of nanoparticles into bulk films proceeds through two stages. First, the organic capping group volatilizes, "leaving a purely nanocrystalline array of particles in contact with each other"[^14]. This step can be accomplished by simply heating, or by exposing with energetic particles such as electrons, as postulated by Reetz[^20] and others[^21]. Next, additional heat can melt the particles and induce grain growth, thus leading to the formation of a conductive film.

In the work described in chapter three, capped Ag nanoparticles dissolved in various solvents serve as a resist for direct-writing by FIB. Regions exposed by the ion beam are immobilized to the substrate surface, and can survive a subsequent wash step, thus leaving patterned nanoparticles. Subsequent annealing forms a conductive, patterned film. The mechanism for nanoparticle immobilization by ions is not well understood, but is likely similar to the mechanisms proposed for electron beam direct-writing of nanoparticles, where irradiation by the incident particles strips the capping groups, rendering the nanoparticles bound to the substrate and insoluble.
The presence of carbon and other contaminants from the capping chemistry has been shown to adversely affect the conductivity of any fabricated structures. In the case of gas phase organometallic precursors, the proportion of undesired components in fabricated structures can correspond to the precursor stoichiometry, where molecules typically have only one metal atom and many organic atoms. Organometallic precursors with clusters of metal atoms also show impaired conductivities, with the best values observed within one order of magnitude of bulk. To address this problem, uncapped nanoparticles generated by a magnetron-sputtering source have been investigated. Their use as the building blocks for a novel fabrication technique based on electrophotography will be discussed in chapter four.

2.2 Uncapped inorganic nanoparticles

Molecular building blocks free of organic components could potentially facilitate the fabrication of nanostructures with conductivities approaching bulk values. A tool developed by Hellmut Haberland\textsuperscript{22}, known as a Nanocluster Source (Figure 8), combines a magnetron sputter discharge with a gas aggregation source, resulting in an instrument capable of generating an intense beam of ionized clusters suspended in an Ar carrier gas. This tool is sold commercially by Oxford Applied Research. Clusters generated from this source, when accelerated to high kinetic energies, can collide with room temperature substrates to form smooth, strongly adhering films. This process is known as “energetic cluster impact” (ECI), and has been used as a method for thin film deposition and for filling high aspect ratio vias\textsuperscript{23}. “Soft-landing,” or non-accelerated clusters, can also be deposited. Films of such clusters are non-adhering and can be easily removed by wiping. Low energy particles generated without acceleration are the focus of this work.
Aside from contamination, another factor that hinders the wider use of organometallic precursors for general fabrication is the lack of available materials. Stable organometallic chemistries can be difficult to synthesize, and may also degrade in quality over time. In contrast, a wide variety of materials, including metals such as Cu, Au, Ag or Al, semiconductors such as Si, Ge, InP, GaAs, and insulators such as SiO$_2$ can be magnetron sputtered, thus significantly increasing the array of materials available for fabrication as compared to processes that rely on organometallic precursors. The targets used for sputtering can be transported and stored with ease, and do not deteriorate with time, although depending upon the material an initial coating of oxide may need to be removed. As will be discussed in greater detail in chapter four, because these clusters are used to develop charge patterns, they can be utilized directly as sputtered without capping groups, thus making any fabricated structures, theoretically, 100% pure. These properties make clusters generated from the Nanocluster Source considerably more attractive building blocks for general fabrication than their organometallic counterparts.

The Nanocluster Source operates by first generating an Ar plasma at the magnetron discharge head "K," as shown in Figure 9. A discharge voltage of approximately 350 V is required to spark the plasma. Once struck, high-energy Ar atoms sputter target "T", generating neutral and ionized atoms of the target material. Some sputtered atoms are
re-deposited onto the sputter target and discharge head, while the majority are swept into the viscous Ar gas stream. These atoms are decelerated by collision with the Ar gas and cooled as they traverse the aggregation region, which is maintained at low temperature by circulating chilled water. The target “T” and the magnetron magnet “M” are also water-cooled. As atoms are sputtered from the discharge, they undergo a variety of collisions and begin to aggregate if their density in the rare gas is high enough. While most of the sputtered atoms from the target are neutral, collisions between these atoms and the charged species in the discharge, particularly electrons, which are present in high density in the plasma, and Ar⁺ ions, lead to charge transfers and the ionization of the aggregating clusters. The charge distribution for clusters depends upon the material, although the quantity of ionized species is usually high; Haberland reports values of ~60 - 80 % for Al, ~20 - 60 % for Mo, and ~20 - 50 % for Cu. This ionization is crucial for the electrostatic patterning techniques discussed in chapter four.

![Nanocluster Source schematic as described by Haberland et al.](image)

Figure 9: Nanocluster Source schematic as described by Haberland et al.²³

The clusters will continue to grow in size as they traverse the water-cooled aggregation region, first forming dimers and continuing to grow as they collide with other clusters and atoms. Finally, they will pass through apertures A1 and A2 into the deposition chamber.
Two electrostatic plates separated by 5 cm (note shown in Figure 9) are mounted on either side of aperture A2 on the deposition chamber side of the source. The potential of the positive plate can be varied between 0 - 500 V, thus generating an electric field that can be used to separate the charged species in the cluster beam during deposition.

As seen in the first section of this chapter, the size of a nanoparticle can dramatically impact its melting properties. Thus, experiments were conducted to correlate the size of clusters generated from the Nanocluster Source with operating parameters, specifically magnetron power. Once characterized, the source could be tuned to optimal settings for obtaining small, sub-5 nm particles for use during electrostatic patterning. Obtaining small clusters is important not only for melting purposes, but also because the resolution of any fabricated structure will be limited by the size of the building block. Ionized atoms were also considered as a building block for electrostatic patterning, but ultimately ionized nanoclusters were pursued because of the larger number of metal atoms per charge. Particles generated from the Nanocluster Source have a distribution of positive, negative, and neutral clusters, and for most operating conditions have only one charge per cluster. Thus, for the different electrostatic patterning modes introduced in chapter four, a single charge stored in an electret could attract a cluster with hundreds of metal atoms, as opposed to a single ionized atom.

2.3 Nanoparticle sizing

Nanocluster size is dependent upon a variety of operating parameters, including power supplied to the magnetron, the size of the aggregation region (and hence the residence time of the nanoclusters), and also the volumetric rate of Ar gas flow. While all impact the ultimate nanocluster size, the parameter of most influence is the power supplied to the magnetron24. To characterize this relationship, nanoclusters deposited at varying magnetron power were studied by transmission electron microscopy (TEM).

2.3.1 Experimental details

The Nanocluster Source was pumped with a Pfeiffer 500 L/s TMV 521P Turbo Pump to achieve a base pressure on the order of $1 \times 10^{-6}$ Torr. Clusters were deposited into a variety of different chambers, including the chamber of a BOC Edwards evaporator, the chamber of an ISI SEM, and also a smaller 6-way chamber normally used for adapting
various vacuum components. A gate valve separated the Nanocluster Source and the deposition chamber, thus allowing for separate pumping when desired. The ISI and BOC Edwards chambers were pumped with an oil diffusion pump and a turbomolecular pump, respectively, to pressures in the range of $1 \times 10^{-5}$ and $1 \times 10^{-6}$ Torr. When depositing in the 6-way chamber, the Pfeiffer pump on the Nanocluster Source was used to achieve a uniform base pressure throughout the source and the deposition chamber on the order of $1 \times 10^{-6}$ Torr. The separation between the anode and cathode of the magnetron was set at 300 μm, while both the magnetron head and the aggregation region were cooled with de-ionized water maintained at a temperature of 10 °C. Cu targets were used for all experiments.

Experiments were conducted by first loading a TEM grid (copper mesh TEM grids coated with a layer of carbon were obtained from Ladd Research) mounted onto a suitable support into the deposition chamber and aligning it with the apertures of the Nanocluster Source. Then, depending upon the formation, either the deposition chamber alone was pumped, or the entire vacuum system was pumped down to its base pressure. Next, Ar was introduced. All experiments were conducted with an Ar flow of 25 sccm. The pressure in the aggregation region for this flow was measured to be 133 mTorr. The voltage of the power source was then adjusted to approximately 300 V, at which point the Ar plasma typically struck. The total power delivered to the magnetron head was then adjusted to the desired value, at which point the gate valve was raised, thus commencing cluster deposition onto the TEM grid. Power settings within the range of 10 to 60 W were tested. Deposition times varied depending upon the experiment, but typically were under 3 minutes to ensure a sparse film. Once deposition was complete, the gate valve was lowered and the deposition chamber was vented. TEM analysis of deposited films was conducted at the Electron Microscopy Shared Experimental Facility in Building 13 of MIT.

2.3.2 Results

The relationship between magnetron power and cluster size for Cu particles is shown in Figure 10. Because many of the clusters were not circular, but were in fact elliptical and even asymmetric, effective diameters were calculated by modeling particles as ellipses. Standard deviations for each data set are also indicated in Figure 10.
Figure 10: Average effective cluster diameter (nm) as a function of magnetron power (W). Standard deviations for each data set are indicated by the error bars.

At lower magnetron powers, the majority of nanoclusters deposited were monocry stalline. Figure 11 shows a field of clusters deposited at 15 W, where, for the most part, the clusters exhibit one crystal lattice plane. However, as the magnetron power increases, larger numbers of clusters with polycrystalline grain boundaries can be observed. Figure 12 shows an example of a 10 nm cluster deposited at 35 W, where multiple grains can be seen. It can be postulated that during the aggregation process, these polycrystalline agglomerates may be formed through collisions of smaller monocry stalline particles. These polycrystalline clusters may also be formed by the aggregation of smaller clusters on the surface of the TEM grid, as opposed to actual collision while in the carrier gas. Occasionally, strings of clusters, as seen in Figures 13 and 14, can be observed, which appear to have linked after depositing on the surface of the grid. Clusters do have some mobility upon striking the substrate, and could be further agglomerating as the film increases in density. Such agglomerations may also explain the deviations seen in Figure 10, as it is possible that the clusters are more
uniform when emerging from the source, but undergo additional aggregation while on the surface.

**Figure 11:** TEM image of a field of mostly monocrystalline nanoclusters. Clusters were deposited with a magnetron power of 15 W.

**Figure 12:** TEM image of a multigrain cluster deposited with a magnetron power of 35 W.

**Figure 13:** TEM image of multiple, overlapping particles deposited at 20 W.
2.4 Conclusions

Though the size of copper clusters generated by the Nanocluster Source has been characterized as a function of magnetron power, the conductivity of cluster films after depositing and annealing has yet to be studied. Initial experiments indicate that non-accelerated cluster films are somewhat conductive even without annealing, but an extensive characterization has yet to be performed and will be the subject of future work.
3 Direct-Write Processes

3.1 Background

This chapter discusses progress made in the area of direct-writing nanoparticles. This work builds upon previous advances in the patterning of organometallic nanoparticle resists with electron beams by demonstrating that focused ion beams can fabricate structures of similar dimension and conductivity while vastly improving throughput. Structures fabricated here also show an increase in conductivity of approximately three orders of magnitude as compared to previous work for FIB-patterning of a gold cluster compound.

3.1.1 Electron beam direct-writing of nanoparticle thin films

Recent work has shown that nanoparticle precursors can be successfully patterned using direct-write methods. Direct-write techniques are advantageous in that they do not require masks, and also eliminate wasteful etching and evaporation steps. Specifically, electron beams have been used to pattern metal nanoparticles capped with various organic ligands.

Reetz et al. exposed (C$_8$H$_{17}$)$_4$N$^+$Br$^-$-stabilized 2.0 nm Pd clusters with an electron dose of 200,000 µC/cm$^2$, resulting in linewidths of 50 nm and conductivities within one order of magnitude of bulk Pd following an 180 °C anneal. The films used in this work were spun onto GaAs substrates to an initial thickness of 132 nm, which was subsequently reduced to 67 nm following annealing. Reetz et al. speculated that the electron beam irradiation
physically removes or destroys the stabilizing ligand, leading to particle agglomeration and concomitant insolubility.

Lin et al.\textsuperscript{21} patterned films of 5.5 nm Au particles capped with 1-dodecanethiol down to a resolution of about 50 nm. A typical exposure dose was 14,400 μC/cm\textsuperscript{2}. Lin, like Reetz, proposed that the electron beam irradiation strips the organic cap, and evidenced this hypothesis with atomic force microscopy (AFM) data confirming a height differential between exposed and unexposed regions.

Bedson et al.\textsuperscript{25} patterned films of 4 - 4.5 nm Au particles surrounded by a chemisorbed monolayer of hexadecanethiol ligands down to a resolution as fine as 26 nm. The typical dose required to expose such films was 5,400 μC/cm\textsuperscript{2}. Bedson also notes that for films approximating monolayer thickness (<10nm), the properties of the inorganic resist are strongly dependent upon the nature of the substrate, as electrons scattered in the substrate dominate exposure of the clusters. For thicker films (>100nm) exposed with 6 keV electrons, the simulations indicate that electron scattering is largely confined to the cluster film itself\textsuperscript{27}.

Werts et al.\textsuperscript{26} achieve similar results in regard to conductivity and linewidth as Reetz when patterning Langmuir-Blodgett films of two types of alkanethiol-capped gold nanoparticles. Sub-50 nm linewidths were achieved along with conductivities about one order of magnitude less than that of a pristine Langmuir-Blodgett film. Interestingly, Werts found that the sensitivity of the resist depended upon the size of the organic capping agent. 3 nm Au particles were passivated with two types of caps, one an n-hexanethiol (abbreviated as AuC6), the other an n-dodecanethiol (abbreviated as AuC12). The sensitivities of films of these particles were 1600 and 500 μC/cm\textsuperscript{2} for AuC6 and AuC12, respectively. Werts also proposes an alternate mechanism for particle immobilization; instead of stripping the organic ligand, as proposed by Reetz and others, Werts' suggests that the electron beam irradiation is actually cross-linking the organic ligand shells. Werts cites infrared spectrum data following electron beam irradiation as evidence that the organic cap persists, and reasons that for a stripping mechanism the AuC12 should be less sensitive than AuC6, because of the larger organic matter present in AuC12, while experimentally the opposite is observed.
3.1.2 Electron beam direct-writing of uncapped nanoparticles

Briefly, in this work direct-writing of uncapped Cu nanoparticles was attempted. Films of Cu nanoparticles deposited by the Nanocluster Source were exposed with 30 keV electrons, and although high-resolution structures with minimum features in the tens of nanometers were fabricated (Figures 16 and 17), it is believed that such structures are in fact carbon deposits. The possibility of directly patterning such films with energetic beams will be the subject of future work.

![Figure 16: SEM image of a wire bridging two pads coated with Cu clusters.](image1)

![Figure 17: SEM image of arbitrary structures patterned on a Cu cluster film.](image2)

3.1.3 Ion beam lithography

While success has been shown in patterning organometallic nanoparticle films with electron beams, the potential for improvement in throughput, without sacrificing resolution or pattern conductivity, exists for direct-writing nanoparticle resists with ion beams. Because of their much greater mass, ions do not travel as far in a resist as electrons do; consequently the deposited energy (or energy density) is greater for ions over a shorter path length. Thus, if sensitivity is measured as charge input per unit area, then resists have a higher sensitivity to ions than electrons\(^{28}\). Table 1 shows a comparison of exposure doses required for electron beam and ion beam patterning of a negative organic resist, polystyrene, and a positive organic resist, poly(methyl methacrylate) (PMMA).
Table 1: Effect of ion mass on required exposure dose. From Tandon.

<table>
<thead>
<tr>
<th>Resist</th>
<th>Ion</th>
<th>Exposure Dose (ions/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>O⁺</td>
<td>4.3 x 10¹¹</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>He⁺</td>
<td>1.4 x 10¹²</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>H⁺</td>
<td>3.7 x 10¹³</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>e⁻</td>
<td>3.3 x 10¹⁴</td>
</tr>
<tr>
<td>PMMA</td>
<td>Ar⁺</td>
<td>2.0 x 10¹¹</td>
</tr>
<tr>
<td>PMMA</td>
<td>He⁺</td>
<td>5.2 x 10¹¹</td>
</tr>
<tr>
<td>PMMA</td>
<td>H⁺</td>
<td>3.6 x 10¹²</td>
</tr>
<tr>
<td>PMMA</td>
<td>e⁻</td>
<td>3.0 x 10¹⁴</td>
</tr>
</tbody>
</table>

As could be expected, the required exposure dose decreases with increasing ion mass. Ions with greater mass deliver more energy per unit depth, resulting in more efficient energy transfer and thus enhanced resist sensitivity. This increased sensitivity for organic resists, which can be several orders of magnitude greater for heavy ions as compared to electrons, does in fact translate to FIB-patterned organometallic resists, although only several such compounds have been studied.

In 1986 Harriott et al. used 20 keV Ga⁺ ions to pattern films of palladium acetate. A full exposure dose was considered to be between 5 x 10¹⁴ and 10¹⁵ ions/cm², or approximately 80 and 160 μC/cm², respectively. While such doses are significantly lower than any of the electron doses reported in section 3.1.1, the lowest reported sheet resistance after heating at 350 °C was on the order of 10⁵ Ω/cm², a value significantly higher than the Pd structures fabricated by Reetz et al., who report structure resistivities as low as 181 μΩ-cm. Hoffmann et al. and Gierak et al. report even lower ion dose requirements for exposing the gold-cluster compound Au₅₅(PPh₃)₁₂Cl₆. For films of this compound, an ion dose between 1 x 10¹³ and 1 x 10¹⁴ ions/cm², or approximately 2 and 16 μC/cm², was required for exposure. Again, however, the resistivity of fabricated structures was high; the lowest reported resistivity was on the order of 1 x 10⁴ μΩ-cm after annealing at 510 °C for 45 minutes. It should be noted that because resistivity was demonstrated to be a function of ion dose, the lowest resistivity was achieved only when exposing with ~1 x 10¹⁶ ions/cm², or ~1600 μC/cm². Hoffmann et al. also report the FIB direct-writing of an Iridium compound, [Ir₄(CO)₁₁Br][N(C₂H₅)₄].
Here, ion doses within a range of $1.6 \times 10^{15}$ and $3.1 \times 10^{16}$ ions/cm$^2$, or approximately 260 and 5000 µC/cm$^2$, respectively, were used to fabricate structures with resistivities as low as 400 µΩ-cm when heated at 500°C for 45 minutes. Although the resistivity is improved compared to the other discussed FIB direct-write methods, the dose required here is more comparable to electron beam direct-write processes.

As seen in section 3.1.1, electron beam patterning of nanoparticles can be extremely slow, with some resists requiring exposure doses upwards of $10^5$ µC/cm$^2$. While several organometallic compounds have been directly patterned by FIB at significantly lower dose, the subsequent resistivity of fabricated structures was high. Thus, given the potential for improving structure resistivity while maintaining the high throughput of other FIB direct-write processes, ion beam patterning of Ag-capped nanoparticles was attempted.

### 3.2 Experimental details: FIB direct-writing

Two different Ag-capped nanoparticle colloids were utilized in this work. The first material, obtained from Vacuum Metallurgical Inc. Ltd., was initially 30 % Ag by weight in toluene, and was further diluted in hexane to the desired metal content. The second material, obtained from Kovio Inc., contained 40 % Ag by weight, and was dissolved in dibutylether. Again, the Kovio solution was diluted in hexane to the desired metal concentration. Solutions of both material were made with metal concentrations varying from 1 to 20 % Ag by weight. Of the two stock solutions the Kovio material was prepared more recently (September 2003) than the Vacuum Metallurgical material (October 2001).

Substrates used in this work were <100> silicon wafer, both n-type and p-type, and standard laboratory grade glass slides cut into approximately 2.5 x 2.5 cm dies. Before coating with nanoparticles, the substrates were cleaned by first rinsing with isopropyl alcohol, then blow-drying in nitrogen gas, and finally by briefly etching in a reactive oxygen plasma. The plasma cleaning was conducted in an Anatech LTD SP100 plasma asher, operated at an RF power of 50 W for 5 minutes at an oxygen pressure of approximately 1 Torr.
Figure 18 shows a schematic for fabricating one layer of material by FIB direct-writing of nanoparticles. First, a thin film of nanoparticles is spun onto a cleaned substrate at 3000 rpm for 30 seconds. Approximately 10 μL of solution is delivered per coat, and the solution is typically injected once the substrate has already achieved its spin speed of 3000 rpm. Once coated, the substrate is then introduced into the FIB for irradiation.

Experiments in this work were conducted with the Strata™ DB235 source manufactured by FEI Company. The Strata™ DB235 utilizes a Ga⁺ ion beam that can be operated at accelerating voltages up to 30 kV with a probe of varying current and spot size. The ultimate beam current and spot size of the Ga⁺ ion beam is determined by the aperture used, which for the Strata™ DB235 can vary to allow currents ranging from 1 pA to as high as several thousand pA. Patterning was conducted exclusively at 30 kV, to maximize the penetration depth of the ions, while beam currents were varied depending upon the experiment. Typically the 1 pA aperture, which corresponds to a beam current of approximately 3 - 4.5 pA, was used to expose fine features while for large area patterns higher beam currents could be used to decrease write times without sacrificing feature resolution. In such cases, beam currents of 12 pA and 40 pA, which correspond to the 10 pA and 30 pA apertures of the Strata™ DB235, were used. Patterns were designed utilizing the CAD software available on the Strata™ DB235.

Once ion irradiation is complete, the substrate is rinsed in two 10-second hexane baths to remove any unexposed nanoparticles. Finally, to finish the processing the substrate is annealed in an oven at 300 °C for 10 minutes to evaporate any remaining solvent and sinter the nanoparticle film.
3.3 Results and discussion

The goal of this work was to establish the optimal operating parameters for FIB-patterning of Ag-capped nanoparticles and to see how it compared to the direct-write techniques discussed in section 3.1, and also to techniques for patterning from the gas phase such as FIB CVD. The major criteria that define the success for any of these techniques are: (1) throughput; (2) the finest achievable lines; and (3) pattern conductivity. Also of great interest is the ability for such processes to build structures in three dimensions.

3.3.1 Required exposure dose

To test the ion dose required to expose Ag-capped nanoparticles, patterns were irradiated with a range of doses and examined optically and with an environmental SEM (ESEM) manufactured by FEI Company. Because of the high energy of the incident Ga\(^+\) ion beam, it was expected that above some dose, instead of properly exposing the nanoparticles, sputtering would occur. Figures 19 - 22 show an example of a significantly over-exposed pattern; the line dose used here was 0.6 \(\mu\)C/cm with a beam current of 40 pA. Designed as an array of unfilled 5 \(\mu\)m squares, the ion beam has actually etched the desired areas, as shown in Figures 21 and 22, while exposing areas extending as far away as 100 \(\mu\)m from the center of the array, as shown in Figure 19. Indeed, the total exposed area scales somewhat linearly with the dose, as seen in Figure 23, which shows the correlation between ion dosage and the total exposed area for the intended pattern of nine 5 \(\mu\)m squares. The width of the etched line is approximately 130 nm.
Figure 19: Optical image of an array of nine 5 μm squares at 50x. These patterns were exposed with a line dose of 0.6 μC/cm, with the over-exposed regions extending out as far as 100 μm away from the center of the pattern.

Figure 20: Optical image of the same array as in Figure 19 at 100x.

Figure 21: SEM image of one of the squares shown in Figure 19.

Figure 22: A further magnified SEM image of an etched line in the nanoparticle resist. The linewidth is approximately 130 nm.
Figure 23: Correlation between the ion dosage delivered to each structure in an array of nine 5 μm squares and the total exposed area.

As shown in Figure 24, a pattern exposed with a line dose of $2 \times 10^{-3} \mu$C/cm still induces an etched region corresponding to the incident ion beam with some over-exposed areas extending several hundred nanometers outwards. This is likely due to backscattered and secondary electron scattering. It was found, however, that using lower beam currents can mitigate this sputtering effect.

Figure 24: SEM image of a line exposed with a dose of $2 \times 10^{-3} \mu$C/cm. A thin milled region can be seen in the center of the pattern.
Figures 25 and 26 show a line patterned with a dose of $2 \times 10^{-4}$ $\mu$C/cm, which corresponds to an area dose of approximately 10 $\mu$C/cm$^2$, using a 40 pA probe. Area doses for patterned lines are calculated by dividing the line dose by the measured linewidth. The features here are still slightly over-exposed, but do not exhibit signs of etching. The spurious particles observed throughout the background of the pattern are most likely artifacts from the washing process.

Figure 25: SEM image of a line exposed with a dose of $2 \times 10^{-4}$ $\mu$C/cm.

Figure 26: A further magnified SEM image of the same line shown in Figure 25.

It is also of note that the over-exposed regions are not initially visible after FIB exposure and can only be seen after the wash step, as shown in Figures 27 and 28. This is not surprising as the mechanism for over-exposure is attributable largely to the scattering of backscattered and secondary electrons from the resist and substrate within the volume of the film, with some smaller contribution due to scattered ions.

Figure 27: Optical image of a series of lines after FIB exposure.

Figure 28: Optical image of the same set of lines shown in Figure 27 after washing.
Ultimately, the ion dose required to properly expose Ag-capped nanoparticles was found to be in the range of 1-10 $\mu$C/cm$^2$. Below 1 $\mu$C/cm$^2$, the nanoparticles can be easily washed off during the hexane rinse, while the onset of over-exposure occurs at ~10 $\mu$C/cm$^2$. Figures 29-32 show examples of some test structures fabricated by FIB-direct writing. Note that these samples are imaged before annealing.

The required dose can be tuned depending upon the types of desired patterns. For most patterns, an ion dose of 5 $\mu$C/cm$^2$ was sufficient to bind the nanoparticles to the substrate without over-exposure. The doses required for exposure were consistent for varying beam currents; thus, for larger area patterns a beam with an increased probe diameter could be used to decrease the overall process time. Beam currents of 40 pA
were commonly used to expose large areas, while for fine lines the smallest aperture, which corresponded to a beam current of approximately 3 - 4.5 pA, was used.

### 3.3.2 Resist sensitivity

To refine the idea of the required exposure dose, experiments were conducted to determine the sensitivity of the resist. As the dose increases, the thickness of patterned structures should also increase until at some dose the entire thickness of the resist has been exposed. The sensitivity of the resist can then be defined as the dose at which half the thickness of the resist is preserved. Thus, to determine the relationship between structure thickness and dose, wires 5 μm wide and 100 μm long were patterned with doses ranging from 1 to 19 μC/cm². Figures 33 and 34 show a set of nine wires with doses ranging from 3 (far left of Figure 33) to 19 μC/cm² (far right of Figure 34), respectively. Note that the structure patterned with a dose of 1 μC/cm² has released and been washed from the substrate, and that generally structures patterned with lower doses did not adhere well after rinsing.

![Figure 33](image1.png) **Figure 33:** Optical image of a series of 5 x 100 μm lines. The dose used to expose each line increases by increments of 2 μC/cm² from left to right, starting with a dose of 3 μC/cm² for the leftmost structure.

![Figure 34](image2.png) **Figure 34:** Optical image of a series of 5 x 100 μm lines. The dose used to expose each line increases by increments of 2 μC/cm² from left to right, starting with a dose of 11 μC/cm² for the leftmost structure.

Once patterned, the height of each structure was measured by AFM. The relationship between dose and structure height is shown in Figure 35, where the error bars indicate the standard deviation for each data set. The structure height appears to level off at approximately 50 nm for a dose of 9 μC/cm²; thus, if we assume 50 nm to be the full thickness of the resist, then the dose corresponding to the exposure of half the thickness of the resist, i.e. the sensitivity, is 5 μC/cm².
Figure 35: The relationship between dose and the heights of 5 x 100 μm structures fabricated by FIB direct-writing. The height of fabricated structures levels off at approximately 50 nm, which is assumed to be the thickness of the resist. The sensitivity is the dose at which half the thickness of the resist, or 25 nm shown here, is preserved. Thus, the sensitivity can be approximated to be 5 μC/cm².

3.3.3 Minimum features
As is always of great interest for any lithographic technique, the limits of resolution were tested for FIB-patterning of Ag nanoparticles. Sub-micron linewidths are easily achievable, and features down to 100 nm can be fabricated with repeatability. Figure 36 shows a series of nested wires with 160 nm linewidths separated by a gap of ~830 nm. Figure 37 shows a similar series of wires with a finer pitch of ~400-450 nm and linewidths of 100 nm.
Figure 36: SEM image of FIB-patterned Ag. The lines have a width of ~160 nm and a pitch of ~830 nm.

Figure 37: SEM image of FIB-patterned Ag. The lines have a width of 100 nm and a pitch of ~400-450 nm.
A significant factor that can impact the resolution of any electron beam-mediated lithographic process is backscattered radiation from the substrate. As seen, for example, in Figure 38, secondary and backscattered electrons affected the sharpness of lines patterned by electron beam direct-writing nanoparticles\textsuperscript{11}. In contrast, at the proper exposure dose, the backscattering of ions is negligible. Secondary electrons that are backscattered from the substrate during ion beam irradiation have very low energies ($\sim 15$ eV) and have ranges of only fractions of a nanometer\textsuperscript{29}. Thus, the energy deposited by each incident ion will tend to affect a smaller region of the resist as compared to an electron, leading to potential improvements in edge roughness and overall pattern sharpness.

![Figure 38: SEM image of fine lines fabricated by electron beam direct-writing of nanoparticles. From Griffith et al.\textsuperscript{11}](image)

It is of note that for fine features, lower doses are often insufficient to bind the exposed material and lift-off during the solvent wash can occur. Figure 39 is an SEM image of lines patterned with a dose of $8.5 \times 10^{-5}$ $\mu$C/cm, which corresponds to an area dose of $\sim 7$ $\mu$C/cm\textsuperscript{2}. To ensure the binding of such features, doses on the order of $10$ $\mu$C/cm\textsuperscript{2} can still be used without significantly impacting feature resolution. The relationship between dose and linewidth for fine features is only roughly understood and demands greater study. The problem of having structures survive a wash step when patterned at low doses is commonly observed in nanoparticle direct-write processes\textsuperscript{11, 12, 20, 25, 31}. 

3 Direct-Write Processes
3.3.4 The role of film thickness

A crucial parameter for FIB-patterning of nanoparticles is the thickness of the resist used. Variations in film thickness greatly affect whether or not a pattern will bind to the substrate or be lifted off during the rinse. Figures 40 and 41 show an example of features patterned in a film with metal content of 10 % Ag by weight before and after the wash step.

When the film thickness exceeds the penetration depth of the ion beam, patterns may be exposed such that they are visible optically, as in the case of Figure 40, but in reality are not immobilized on the substrate surface. Because the ions have only penetrated partially through the resist, and not down to the substrate, a layer of unexposed material persists below the exposed pattern. Consequently, during the wash step the solvent
dissolves the particles beneath the exposed structure, thus causing it to release and wash from the substrate. The occurrence of this phenomenon at even low dilutions of metal is not surprising given the potentially shallow penetration depths of a 30 keV Ga\textsuperscript{+} ion beam in a nanoparticle resist. Table 2 shows the experimentally observed penetration depth of Ga\textsuperscript{+} ions and several other ions in organic resists.

**Table 2**: Penetration range of ions in organic resists. From Jensen\textsuperscript{36}.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Energy (keV)</th>
<th>Range (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga\textsuperscript{+}</td>
<td>40</td>
<td>46</td>
</tr>
<tr>
<td>Ga\textsuperscript{+}</td>
<td>55</td>
<td>60</td>
</tr>
<tr>
<td>Ga\textsuperscript{+}</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>Ar\textsuperscript{+}</td>
<td>120</td>
<td>200</td>
</tr>
<tr>
<td>Li\textsuperscript{+}</td>
<td>100</td>
<td>850</td>
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<tr>
<td>He\textsuperscript{+}</td>
<td>40</td>
<td>440</td>
</tr>
<tr>
<td>H\textsuperscript{+}</td>
<td>40</td>
<td>520</td>
</tr>
<tr>
<td>H\textsuperscript{+}</td>
<td>120</td>
<td>1120</td>
</tr>
</tbody>
</table>

Given the small penetration ranges of 40 to 120 keV Ga\textsuperscript{+} ions in organic resists, the depth of penetration for the 30 keV Ga\textsuperscript{+} ions used in this work into a nanoparticle resist was not expected to be very deep, e.g. about 30 nm. In order to glean a rough sense of how deeply the Ga\textsuperscript{+} ions penetrated into Ag thin films, a relationship between film thickness and the metal content of the solution needed to be determined. Spin conditions and substrate preparation were the same for all experiments, so the film thickness was ultimately determined by the percent weight of Ag in the solution. Atomic force microscopy (AFM) and stylus profilometry were attempted to measure step heights from scratches in nanoparticle films, but because of the softness of the material the probes used would easily scratch or drag particles across the surface, thus giving erroneous data. A rough sense of the penetration was obtained by measuring already washed structures, which were significantly easier to image by AFM. The thickest structures obtained after washing that were not over-exposed or discernibly released had a height of approximately 50 nm; thus, it can inferred that at most, the 30 keV Ga\textsuperscript{+} ions were penetrating a depth of 50 nm into the film. Structures patterned in films with a thickness greater than 50 nm can be expected to release to some degree, and as metal
content and thus film thickness increases the frequency and degree of release will likewise go up.

The degree to which patterns were lifted-off and the frequency of their occurrence is described qualitatively in Table 3. It can be surmised that the critical thickness of 50 nm likely corresponds to a metal content of approximately 3 %, as the onset of likely structure release occurs at that metal concentration. For metal content above 10 %, the probability of total pattern lift-off was very high; more than 50 different patterns exposed in films with 19 % metal content were washed off without exception. As the metal content decreased below 10 % the frequency and degree of the lift-off varied. For example, the released structures shown in Figure 41 were among 7 of 24 patterns still found on the substrate for a film composed of 10 % Ag.

Table 3: Description of the frequency and degree of lift-off for films of varying metal content.

<table>
<thead>
<tr>
<th>% Ag by weight</th>
<th>Frequency of lift-off</th>
<th>Degree of lift-off</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.54</td>
<td>Only at low doses, particularly for fine patterns</td>
<td>Usually partially lifted thus leading to pattern deformation, rarely completely washed</td>
</tr>
<tr>
<td>2.1</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>2.5</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>2.9</td>
<td>Often, regardless of dose</td>
<td>Usually partially, occasionally completely</td>
</tr>
<tr>
<td>3.9</td>
<td>Almost always, regardless of dose</td>
<td>&quot;</td>
</tr>
<tr>
<td>5</td>
<td>Always</td>
<td>&quot;</td>
</tr>
<tr>
<td>10</td>
<td>&quot;</td>
<td>Occasionally partially, usually completely</td>
</tr>
<tr>
<td>19</td>
<td>&quot;</td>
<td>Completely</td>
</tr>
</tbody>
</table>

The degree to which structures release is relatively uniform for a specific dose and film thickness. However, for a given film thickness, structures patterned with higher doses have a greater probability of surviving the wash step. This is because at higher doses, there is increased scattering of ions and electrons thus allowing the exposure of nanoparticles deeper into the resist layer than at lower doses.
Figures 42-45 show additional examples of released structures. As will be discussed in
greater detail in section 3.4.3, occasionally structures can fold into shapes with three-
dimensional character.

Figure 42: SEM image of what was originally an un-filled square which partially released
during the rinse.

Figure 43: Optical image of a partially released structure patterned from a film with 4 % Ag by weight.

Figure 44: Optical image of a wire released from the edge of a gold pad.

Figure 45: Optical image of a folded, released structure.

Structures that experience even small amounts of release will lose their sharpness and
may cause stresses throughout the pattern thus leading to cracks and fissures. Such
effects increase in frequency with increasing metal concentration. Figure 46 shows an
example of a pattern fabricated at a dose of 5 μC/cm² from a film composed of 4.8 % Ag.
The formation of these “mud cracks” may also be attributable to the decrease in film
volume during the solvent rinse$^{34}$. As seen in Figure 47, biaxial tensile stresses arise
within the film because the shrinkage is constrained by the substrate. To relieve this
stress, fissures can propagate. Gierak et al.$^{31}$ suggest that these cracks are caused by
penetration of the solvent into the resist layer during development.
To avoid the cracking associated with structure release, thinner films should be used to allow for greater ion penetration. However, as seen in the next section, there are significant tradeoffs to consider, as the conductivity of fabricated structures is also highly correlated to the thickness of the nanoparticle film.

### 3.3.5 Conductivity

In order to test the conductivity of FIB-exposed structures, patterns designed for four-point probe measurements were fabricated. An example of one such structure is shown in Figure 48. Resistance values were calculated by first measuring the voltage
difference between pads labeled 2 and 3 in Figure 48 while injecting current from pad 4 to pad 1. By plotting the $I-V$ curve from the measured data a resistance can be obtained for the red region indicated in Figure 48. The resistivity can then be calculated using the following equation:

$$\rho = \frac{RhW}{L}$$

where $R$ is resistance, $h$ is height, $W$ is width and $L$ is length. To insure the validity of the calculated resistivities the length of the red region in Figure 48, here shown to be 75 $\mu$m, was varied for different test structures from 25 to 200 $\mu$m. The width was set at 25 $\mu$m, while the height varied depending upon the initial film thickness. Structures decrease in height by as much as 50 % during the anneal step due to solvent evaporation, organic cap volatilization, and overall material densification. The heights of the various test structures were measured by AFM.

**Figure 48:** Optical image of a FIB-patterned four-point probe structure used to test material conductivity. Current is passed through the pads labeled 1 and 4 while the voltage difference is measured between pads 2 and 3. From the measurements the resistance of the region indicated in red can be plotted.
An example of an $I$-$V$ curve for a region with a length of 50 $\mu$m and a height of ~30 nm is shown in Figure 49. The resistance here was 192 $\Omega$, and the calculated resistivity was 288 $\mu\Omega$-cm as compared to a resistivity of 1.589 $\mu\Omega$-cm for bulk silver. Figure 50 shows that the resistance does in fact scale approximately linearly with increasing wire length. This data is for test structures patterned from a film of 3.8 $\%$ Ag by weight.

Figure 49: $I$-$V$ curve for a 25 x 50 $\mu$m resistor with a height of 30 nm.

Figure 50: Plot showing that resistance does in fact scale linearly with wire length.
Overall, the lowest resistivities were calculated for test structures fabricated with higher metal concentrations, and thus greater film thickness. Overall the fresher Kovio solutions gave better resistivity values, even at lower metal concentrations. Table 4 shows a comparison of resistivities calculated for test structures at various metal concentrations, with the type of solution used, either Vacuum Metallurgical or Kovio, indicated. The large deviation can in part be attributed to poor contact between the probe tips and the patterned structures, as single-layer structures are quite fragile and can be easily scratched or damaged.

Table 4: Comparison of calculated resistivities for structures with varying metal concentration.

<table>
<thead>
<tr>
<th>% Ag by weight</th>
<th>Resistivity (μΩ-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>≤ 2.9 (VM)</td>
<td>Not Conductive</td>
</tr>
<tr>
<td>≤ 2.66 (Kovio)</td>
<td>Not Conductive</td>
</tr>
<tr>
<td>3.8 (Kovio)</td>
<td>355 ± 112</td>
</tr>
<tr>
<td>4.8 (Kovio)</td>
<td>318 ± 87</td>
</tr>
<tr>
<td>5 (VM)</td>
<td>569 ± 365</td>
</tr>
</tbody>
</table>

The onset of conductivity occurred for annealed structures approximately 25 nm thick. Test structures with thicknesses below 25 nm often appeared grainy in texture optically, and when examined by AFM were found to be discontinuous and composed of isolated aggregates, as shown in Figure 51, where a film of 1.54 % Ag was used.

Figure 51: AFM image of an area of a FIB-patterned structure showing film discontinuity. The film thickness here was approximately 20 nm.
Given the discontinuous nature of these films it is not surprising that such structures were not conductive. However, as the films increase in thickness, it is believed that the stacking of such agglomerates leads to increased connectivity and thus increased conductivity.

It should be noted that the best resistivities obtained for this single-layer process, approximately 300 $\mu\Omega$-cm, are still two orders of magnitude larger than bulk, a result that is not consistent with other work patterning Ag nanoparticles by electron beam direct-writing, which report a value of 67 $\mu\Omega$-cm$^{11}$. One possible explanation is that the Ga$^+$ ions used may be implanting into the material and affecting the crystallinity of any grains present. To test the concentration of any Ga implanted in FIB-patterned structures, energy dispersive X-ray spectroscopy (EDX) was conducted. Figure 52 shows spectra of an Ag nanoparticle film immediately after being spun on a silicon wafer (top) and after exposure to a FIB and rinsing in hexane (bottom). Analysis was performed using a SEM at an accelerating voltage of 5 kV. Such low energy electrons were used to better ascertain the composition of material closer to the surface of the substrate.
Figure 52: Energy dispersive X-ray spectroscopy measurements for an Ag nanoparticle film before FIB exposure (top) and afterwards (bottom). Note that the sample was also washed following FIB exposure. Both spectra were taken with an SEM at an accelerating voltage of 5 kV.

The presence of Ga could not be detected by EDX, although the significant presence of carbon is noteworthy. The carbon content in the film decreases noticeably because of the hexane rinse, but clearly still impacts the composition of the film. As with any process involving organometallic precursors, carbon content always affects the purity of fabricated structures. In this regard, FIB direct-writing is no different. However, because the Vacuum Metallurgical material used in this work is the same as that used by Griffith et al.\textsuperscript{10,11}, the possibility that the FIB direct-write process somehow facilitates greater carbon content does not seem likely, as the electron beam process uses the same set of steps. A possible explanation may be that even concentrations of Ga not discernable by EDX still disrupt film crystallinity. Another possibility could be that even for low doses, some sputtering is occurring and inducing the types of discontinuities observed in Figure 51. The most likely explanation, however, is simply that the fabricated structures are not sufficiently thick. In the electron beam direct-write process, much thicker structures can
be fabricated due to the greater penetration depth of electrons. In this work, the thickest structures, though conductive, often exhibit undesirable artifacts. For example, the test structure shown in Figure 53 was conductive, with a resistivity of 320 μΩ-cm, while the structure shown in Figure 54 was not. In order to obtain conductive structures that preserve the crispness of the patterning, and in attempt to improve conductivity values as compared to single-layer structures, stacks of low metal concentration films were patterned and annealed. This process of multi-layer fabrication will be discussed in greater detail in section 3.3.6.

**Figure 53**: Optical image of an annealed structure with an initial metal concentration of 4.8 %.

**Figure 54**: Optical image of an annealed structure with an initial metal concentration of 2.66 %.

Figures 55 and 56 show a two-layer test structure fabricated from a Kovio solution with a metal concentration of 2.66 % before and after annealing. Again, as noted above, a single layer of material fabricated from a solution of 2.66 % Ag was not conductive; however, a structure composed of two such layers stacked in succession was, in fact, conductive.
The resistivity of stacked structures improved markedly as compared to single-layer structures. In order to minimize errors in the resistivity calculation due to the alignment problems inherent in the multi-layer process, larger area test structures, with widths of 50 μm (as opposed to the 25 μm wide structures shown in 55 and 56) and lengths varied between 50 and 200 μm, were utilized. The resistivity calculated for such two-layer structures was 15.3 ± 1.9 μΩ-cm, a reduction in resistivity of approximately 20 times as compared to the most conductive single-layer structures. This value is approximately one order of magnitude larger than the resistivity of bulk Ag, 1.589 μΩ-cm. Three-layer structures were also fabricated, and had a calculated resistivity of 16.1 ± 3.5 μΩ-cm, which agrees well with the resistivity value for two-layer structures. This result suggests that the structures are now sufficiently thick such that any additional layering will have a negligible improvement on conductivity. Figure 57 shows an I-V curve for both a two-layer and a three-layer structure. Figure 58 is a plot of the resistance of two-layer and three-layer structures as a function of wire length, verifying that a linear relationship exists. Figure 59 shows an I-V curve for a two-layer structure (here with a linewidth of 25 μm), indicating that the wire has been blown at a current of approximately 30 mA. Figure 60 shows a magnified image of the overlapping region of two test structures with a failure point after being blown out.
Figure 57: $I-V$ curves for a two-layer and three-layer structure fabricated by FIB direct-writing.

Figure 58: A plot showing that resistance increases linearly as a function of wire length for both two-layer and three-layer structures.
**Figure 59**: An $I$-$V$ curve for a two-layer structure. The structure fails at a current of $\approx 30$ mA.

**Figure 60**: Optical image taken at 100x of the failure point of a two-layer structure after being blown out.
3.3.6 Multi-layer structures
As stated previously, the role of film thickness is critical for FIB direct-writing of nanoparticles. If the film is too thick, the ion beam may not penetrate deeply enough into the resist to immobilize the nanoparticles; if the film is too thin, the final annealed structure may not be conductive. While the best solution to this problem is to use ions more energetic than the 30 keV Ga⁺ ions used in this work, thus increasing the penetration depth and allowing the use of thicker films, an alternate strategy relying on the fabrication of multiple layer structures was explored.

Two different process routes were used for building multi-layer structures, as shown in Figures 61 and 62. In the first route, the process for fabricating a single-layer structure, as outlined in Figure 18, was essentially repeated multiple times by spinning and patterning additional layers of nanoparticles with a rinse step after each FIB exposure. The processing was completed with a global anneal. The second route, as shown in Figure 62, is similar except that a rinse step was not utilized between layers. This particular method of processing is of interest because of its potential application to a complete in-situ process, as will be discussed in section 3.4.1.

Figure 61: Schematic for the fabrication of multiple layer structures. Here, the substrate is washed before each solution coat step.
The key difficulty for both of these processes is alignment. To address this problem, FIB patterns were designed with sacrificial fiducials. Because normal imaging with a FIB readily exposes the nanoparticle film, the alignment process itself is inherently destructive; thus, features not desired in the final pattern were used for alignment. Once the image in the CAD file was properly aligned to the sacrificial fiducial while live imaging, the ion beam was blanked and the stage was then moved to an unviewed region, whereupon the desired pattern was exposed. Depending upon the pattern, an additional series of stage moves could be performed relative to the positioning of the initial alignment mark. For such a process, patterns exposed further from the initial mark become progressively more misaligned, particularly if multiple stage moves are required. Utilizing a design with many fiducial marks can help to augment the accuracy of the overall pattern, although obviously time spent manually aligning to such features can markedly increase the overall process time. For the alignment of initial layers, fiducials could also be directly milled into the substrate.

Figure 63 details the initial stages of the process used for fabricating a five-layer structure. First, an alignment mark was milled directly into a silicon wafer, as seen in Figure 63(a), followed by the spin-coating of the substrate with a thin film of nanoparticles. Next, the fiducial was imaged live with the FIB, and an image of the desired pattern, four 50 μm squares, was positioned over the visible milled cross. Once aligned properly, the pattern was then exposed. Note that in (c) and (d), a rectangle corresponding to the field of view of the FIB can be seen both before and after the wash. In steps (e), (f), and (g), the coat, expose, and wash steps were repeated for a second
layer, where this time an unfilled square structure with a linewidth of 10 μm was patterned. As seen in (g), even after just two processing stages the initial milled cross is no longer discernable, and the subsequent layers have been damaged by both the normal processing as well as the live viewing during alignment. While still possible to align to, the difficulty of such a procedure increases with successive layers. Thus, having additional fiducials, which can be utilized as the initial marks wear, becomes essential for structures with many layers. Figure 63(i) shows the alignment mark after the five stages of processing are complete.

Figure 63: Optical images of various processing stages for a five-layer structure as viewed at a sacrificial fiducial. (a) An alignment cross milled into silicon. (b) The same alignment mark coated with a film of nanoparticles which is then: (c) exposed, (d) washed, (e) re-coated, (f) exposed again, (g) washed, and finally (h) re-coated. (i) shows the alignment mark once the five stages of processing have been completed.

Figure 64 shows a similar progression as in Figure 63, except for an actual desired structure. In (a), the first set of 50 μm squares has been exposed and washed; in (b)-(d), another round of processing has produced the unfilled 10 μm-wide square structure;
(e)-(g) show the next series of steps which produce a second stack of four \(50 \mu m\) squares, and finally (h) and (i) show the structure after a third and fourth stack of \(50 \mu m\) squares are patterned, resulting in a structure with five total layers.

**Figure 64**: Optical images of various processing stages for a five-layer structure. (a) Four \(50 \mu m\) squares are exposed and washed, then (b) re-coated, (c) exposed, (d) washed, (e) re-coated, (f) exposed again, and (g) washed to form a three-layer structure. (h) and (i) show the structure after processing its fourth and fifth layers, respectively.

This structure was fabricated three stage moves away from the sacrificial fiducial used for alignment, resulting in placement errors of several \(\mu m\). These errors can be seen more prominently in Figures 65 and 66. It is noteworthy that because liquid films were used, no planarization was required between layers; the liquid relies on gravity to conform to layers below, thus eliminating the need for any chemical mechanical polishing or other such procedures.
Figure 65. Optical image of a five-layer structure fabricated by FIB-patterning of Ag. Misalignment errors up to several μm can be observed.

Figure 66. AFM image of the same five-layer structure shown in Figure 65.

The second mode of fabrication outlined in Figure 62 was used to fabricate the simple two-layer test structures shown in Figures 55, 56 and 60. As seen in Figure 67, once a first layer is exposed it is then (a) coated without a wash step, (b) re-exposed, (c) washed, and finally (d) annealed. Notice again the alignment errors present.
Figure 67: Optical images of various processing stages for a two-layer structure fabricated as described in Figure 62, where only a single global wash and anneal are used. Once an initial pattern is exposed it is (a) coated without washing, then (b) re-exposed, (c) washed, and (d) annealed to complete the processing.

When fabricating structures via the coat/pattern/coat/pattern process outlined in Figure 62, it is interesting to note that for thick films, as commonly seen for single-layer patterns, structures not immobilized to the layer below can be released during the spin-coating process instead of during the wash. Figure 68 shows four 50 μm squares exposed at an alignment mark which is subsequently coated with a second layer of resist. As seen in Figure 69, the four squares, which were not properly bound to the substrate below, were released while spin-coating. Thus, the spin-coating step can act as a virtual wash for any unbound structures. To avoid such structure release the coat/pattern/coat/pattern process, like the single-layer process, must use thin films.
When making multi-layer structures it can be helpful to use higher beam currents than what would eventually be used in the actual patterning step to live image the alignment mark. Higher beam currents can improve the visualization of resist-coated structures by both sputtering away the coating and also by increasing the signal to the detectors in the FIB as a result of the greater number of scattered electrons and ions.

3.4 Future work

In this section several topics of interest for future work will be briefly discussed, namely the in-situ fabrication of nanostructures, the possibility of fabricating unsupported structures, and also the potential for using FIB direct-write to fabricate folding three-dimensional structures.

3.4.1: In-situ fabrication

With the exception of FIB CVD, all of the other processes referenced in this work capable of building structures with three-dimensions, including all standard silicon processing, require multiple steps that utilize high vacuum (HV) or ultra high vacuum (UHV) equipment. Wafers must be repeatedly loaded in and out of vacuum, thus requiring, in the case of silicon processing, exorbitantly costly clean rooms to protect substrates from contamination. Similarly, the direct-write experiments conducted in this work and by Griffith et al.\textsuperscript{11} also required a pump down for every desired layer of material. A solution to this problem would be an all encompassing machine capable of fabricating a completed three-dimensional device in a single pump down, thus side-
stepping the need for exposure to the ambient environment, and in the case of FIB direct-write, eliminating the need to align structures when building multiple layers. To that end, fellow graduate student Vikas Anant has developed a device capable delivering, in-situ, droplets of nanoparticles on demand. The setup is shown in Figure 70. The device operates simply by pushing out a small volume of nanoparticle solution with a purge of nitrogen gas through a thin delivery tube to the substrate. A variation of this device also in progress relies upon an electrospray method to deliver coatings of nanoparticle solutions while in vacuum. Future work will involve incorporating these devices with the coat/pattern/coat/pattern mode of FIB direct-write to build structures in a single pump down. Again, alignment is no longer necessary for a well-designed structure. For example, the five-layer structure shown in Figures 65 - 66 could potentially be made without noticeable stacking errors by coating, patterning, and then without moving the stage coating and patterning again. Such a set-up would be an ideal method for fabricating three-dimensional structures by FIB direct-writing of nanoparticles.

![Figure 70. Optical image of the preliminary setup for in-situ delivery of nanoparticle solutions.](image)

### 3.4.2 Unsupported structures

A novel design for the fabrication of unsupported structures is proposed here to take advantage of the shallow penetration depth of ions in a nanoparticle resist. As shown in Figure 71, an unsupported, freestanding bridge could potentially be fabricated by patterning a layer of nanoparticles in a second coating of resist that spans two anchor
structures in the layer below. If the resist can be tuned to the approximate height of ion beam penetration, then the resist will be exposed only in the area above the two supports in the second layer of resist and leave the region between the supports in the first layer of resist unexposed. Thus, during a global rinse step, the material beneath the spanning structure would be cleared, leaving a freestanding bridge. Such a structure would be extremely difficult to fabricate via an electron beam mediated direct-write process, as electrons have penetration depths with significantly greater range than do ions.

Figure 71. Proposed schematic for the fabrication of unsupported structures. Steps 1-3 follow for a standard repeated coat/pattern process, except in step 4 a structure spanning two supports is exposed in the second layer of resist. Because of the shallow penetration depth of the ion beam, the region beneath the bridge would be unexposed, leaving behind a freestanding structure after a global rinse step.

3.4.3: Folded structures
When examining patterns released during the hexane rinse by SEM, a number of fascinating folded structures were found. Figure 72 displays a number of such partially released structures in a mosaic. Originally un-filled squares, the patterns shown below have collapsed during the wash step and folded, presumably to reach their most energetically stable state, to create roughly three-dimensional formations. When examined, the manner in which many of the structures have assembled share common features, such as similar fracture and re-bonding points. In fact, it may be possible to force such structures to fold into certain desired shapes with repeatability by designing clever 2D FIB patterns. Such structures could be novel in their parallels to protein folding, and also in the study of self-assembly in general. Figure 73 shows a magnified image of one such folded shape.
Figure 72: A mosaic of SEM images of various structures released from the substrate and then folded into shapes with some three-dimensional character.

Figure 73. SEM image of a portion of a folded release structure.
3.5 Conclusions

Of key significance for this process is the demonstrated vast increase in speed compared to electron beam mediated direct-write methods. As seen in Table 5, the dose required for FIB direct-writing of nanoparticles is only 5 μC/cm², a value several of orders of magnitude lower than those reported for any electron beam direct-write processes to date. As a result, speeds of fabrication can increase dramatically. Typical doses for FIB direct-writing of nanoparticles are also more than an order of magnitude lower than other established lithographic techniques such as electron beam patterning of PMMA and FIB CVD of organometallic gases. While FIB direct-writing of $\text{Au}_{55} (\text{PPh}_3)_{12} \text{Cl}_6$ and palladium acetate have comparable write speeds, the resistivity of structures fabricated utilizing those techniques is several orders of magnitude higher than those fabricated by FIB direct-writing of Ag-capped nanoparticles.

Table 5: Comparison of typical exposure doses and resistivity values for various resists.

<table>
<thead>
<tr>
<th>Resist</th>
<th>Exposure Method</th>
<th>Typical Exposure Dose (μC/cm²)</th>
<th>Resistivity (μΩ-cm)</th>
<th>Resistivity-Dose (μΩ-μC/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{(C}_8\text{H}_7\text{)}_4\text{N'Br}^{-} \text{ stabilized Pd nanoparticles}^{20}$</td>
<td>EB direct-write</td>
<td>200,000</td>
<td>181</td>
<td>36,200,000</td>
</tr>
<tr>
<td>1-dodecanethiol - stabilized Au nanoparticles$^{21}$</td>
<td>EB direct-write</td>
<td>7,000-14,400</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>$\text{(C}<em>{16}\text{H}</em>{33}\text{S})^{-} \text{ stabilized Au nanoparticles}^{25}$</td>
<td>EB direct-write</td>
<td>5,400</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>Alkanethiol - stabilized Au nanoparticles$^{26}$</td>
<td>EB direct-write</td>
<td>1,000 and 3,000</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>Ag-capped nanoparticles$^{11}$</td>
<td>EB direct-write</td>
<td>1200</td>
<td>67</td>
<td>80,400</td>
</tr>
<tr>
<td>Organometallic gas: $((\text{CH}_3)\text{C}_2\text{H}_5\text{C}_5\text{H}<em>9\text{Pt})</em>{35, 5}$</td>
<td>FIB CVD</td>
<td>1600</td>
<td>70 - 700</td>
<td>112,000 - 1,120,000</td>
</tr>
<tr>
<td>[Ir(<em>4)(CO)(</em>{11})Br([\text{N(C}_2\text{H}_5)_4])(^{32}$</td>
<td>FIB direct-write</td>
<td>250-5000</td>
<td>400</td>
<td>100,000 - 2,000,000</td>
</tr>
<tr>
<td>PMMA</td>
<td>EB (positive resist)</td>
<td>130</td>
<td>Not conductive</td>
<td>-</td>
</tr>
<tr>
<td>$[\text{Pd(O}_2\text{CCH}_3)_2]_3$(^{30}$</td>
<td>FIB direct-write</td>
<td>80-160</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Au}_{55} (\text{PPh}<em>3)</em>{12} \text{Cl}_6$(^{12}$</td>
<td>FIB direct-write</td>
<td>2-16 / 1600</td>
<td>N/A / -10,000</td>
<td>- / 16,000,000</td>
</tr>
<tr>
<td>Ag-capped nanoparticles</td>
<td>FIB direct-write</td>
<td>5</td>
<td>318 (one-layer)</td>
<td>1,590</td>
</tr>
<tr>
<td>Ag-capped nanoparticles</td>
<td>FIB direct-write</td>
<td>5</td>
<td>15.3 (two-layers)</td>
<td>77</td>
</tr>
</tbody>
</table>
Clearly, both the required exposure dose and the ultimate resistivity of any patterned structures are key parameters for characterizing any direct-write process. To better appreciate the impact of these factors, we introduce here a new unit of merit obtained by multiplying the required dose and the achieved resistivity, termed the resistivity-dose ($\mu\Omega \cdot \mu\text{C/cm}$). Resistivity-dose values are shown in Table 5 for many of the direct-write processes discussed in this thesis. FIB direct-writing of Ag nanoparticles, even for single-layer processes, has a low resistivity-dose value, indicating that the process rates well in regard to both throughput and structure conductivity. The value of $77 \mu\Omega \cdot \mu\text{C/cm}$ for a two-layer structure is many orders of magnitude lower than the other direct-write processes listed, but needs some correction, as it does not take into account the necessity of multiple layers.

The most important element of FIB direct-writing is of course the resist material itself. While the mechanisms that lead to the increased conductivity and sensitivity of the Ag resist are not fully understood, several conjectures can be made. First and foremost, the Ag particles used in this work are likely composed of hundreds of metal atoms as compared to the iridium and palladium acetate compounds, which have only several metal atoms per molecule, and Au, which has only has tens of metal atoms per molecule. Of course, the increased metal for Ag particles is useful only if the overall ratio of metal to organic material is increased. However, because similar Ga$^+$ ion energies were used in all of the cited works (20 - 30 keV), a cursory comparison of the resistivity of single-layer structures suggests that the Ag material is in fact purer. While purity is important, it is likely that the primary factor that facilitates structure resistivities within an order of magnitude of bulk is the use of multi-layer structures. All FIB direct-write processes (assuming the use of similar Ga$^+$ ion energies) suffer from the same limitation, namely the shallow penetration depth of Ga$^+$ ions. Thus, regardless of the material, the thin structures fabricated by single-layer FIB direct-write will likely be relatively poor conductors. The most important efforts for future work in this area will be the improvement of the multi-layer fabrication process.

Given the rapid fabrication speeds and the relatively low resistivity of fabricated structures, FIB direct-writing of Ag-capped nanoparticles has the potential to be useful not only in the novel direct fabrication of nanostructures, but also as a significantly faster alternative to FIB CVD, a technology relied upon in the chip and mask repair industry.
4 Electrostatic Patterning

4.1 Background

Chester Carlson, a patent lawyer from Queens New York, demonstrated the first xerographic image in his makeshift laboratory on October 22, 1938. Since that time his invention has led to a worldwide copy industry made up of Xerox and other corporations that produces billions and billions of copies each year with total annual revenues in the tens of billions of dollars. An example of a cartridge used in modern electrophotographic technology is shown in Figure 75.

![Figure 74: Text of the first xerographic image ever fashioned, consisting of the date and location of its realization. From Pai et al.][1]

![Figure 75: Canon Inc.'s all-in-one cartridge for electrophotography.][2]

Six basic process steps are required in any electrophotographic device, be it a copy machine or a laser printer[3]. First, a corona discharge, caused by air breakdown,
uniformly charges the surface of a photoreceptor, labeled “exposure development roller” in Figure 75. Next, light reflected from a document (in a copier) or produced by a laser (in a printer) discharges the photoreceptor, producing a latent image. Pigmented polymer particles called toner, which are approximately 10 μm in diameter, are brought into the vicinity of the roller and adhere to the latent image. The developed toner particles are then transferred onto paper, where they are heated and fused. The photosensitive roller is finally discharged and cleaned in preparation for further processing. The resolution achieved in xerography is about 100 μm.

While the electrophotographic process used in xerography has for many years been successful in selective deposition on a macroscopic scale, several groups have used these principles of electrostatic attraction for particle manipulation and fabrication on the submicron scale. Mesquida and Stemmer\textsuperscript{37} have used the conductive tip of an AFM to deposit localized charge patterns in poly(tetra-fluoroethylene) (PTFE) by applying voltage pulses of ±15 - 20 V to the tip. Either positive or negatively charged patterns can be formed. Immersing the substrate into a suspension of 290 nm or 50 nm silica particles subsequently develops these patterns. The resolution of such deposited structures is about 1 μm, an improvement of two orders of magnitude over standard xerography. Figure 76 shows Kelvin force microscopy (KFM) images along and optical images of developed charge patterns.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figures.png}
\caption{(Top) Surface potential images taken by KFM, with the potential ranges of \(-3\) V to \(0\) V for the left image and \(0\) V to \(+3\) V for the right. (Bottom) Light microscope image after development. From Mesquida and Stemmer\textsuperscript{37}.} 
\end{figure}

Jacobs et al.\textsuperscript{38} have been working toward submicron trapping of charge in thin layers of PMMA on n-doped silicon by applying 10 – 20 V between the conductive silicon support
and a patterned gold-coated poly (dimethylsiloxane) stamp. Using such a method they have patterned charges with ~150 nm resolution over areas as large as 1 cm$^2$. These charge patterns have been successfully developed using toner, graphitized carbon, and red iron oxide particles from liquid and gas-phase suspensions.

![Figure 77: Toner-developed charge patterns, by Jacobs et al.](image)

50-µm-wide parallel lines of toner particles, <20 µm in size, are shown.

Fudouzi et al. have been working toward electrostatic particle assembly by developing ion beam induced charge patterns with silica (SiO$_2$) and other polymeric particles. In their process, a CaTiO$_3$ substrate is irradiated with 30 keV Ga$^+$ ions, inducing a positive charge pattern. The substrate is then immersed in a suspension of silica particles for pattern development, and then dipped in a perfluorocarbon solvent for rinsing. Finally, the patterned particles are fixed to the substrate by heat treatment. Surface potentials ranging between 50 and 300 V were achieved for Ga$^+$ ion doses between 10 and 50 nC.

![Figure 78: Fudouzi et al.'s electrostatic particle assembly](image)

(Left) SEM image of positively charged dots on a CaTiO$_3$ substrate. (Right) Optical image of a charge pattern developed with 10 µm polymer particles.
4.2 This work

The overall vision of this work is to develop an entirely in-situ process for the rapid fabrication of high purity nanostructures and devices. Termed 'nanoxerography,' the proposed method utilizes an electron or ion beam to pattern negatively and/or positively charged features into charge-retaining materials, known as electrets, for subsequent development with ionized inorganic nanoclusters. While prior work has shown that particles can be electrostatically assembled on surfaces with micron to sub-micron resolution, each of these processes still requires a substrate transfer step from the charging apparatus to the development site. By mating the Nanocluster Source and the energetic beam source into a single vacuum system, charged nanoclusters may be delivered to the site of fabrication for immediate development of charge patterns, resulting in the manufacture of structures and devices in a single pump down. Furthermore, in this embodiment no solvent or wash step is required, as the process is all additive; that is, material is placed only where desired, as opposed to being subtractively etched or washed, as in traditional silicon processing or in the majority of the direct-write methods discussed in chapter 3. Also, as mentioned in chapter 2, the material set for this tool enables the use of a vast array of building blocks ranging from metals, semiconductors, and insulators, allowing for significant flexibility in the variety of structures that can be fabricated. Figure 79 shows a schematic for such in-situ processing, where charge patterns written by a suite of beams are developed by nanoclusters.
Two embodiments are proposed for such fabrication; in the first, both the energetic beam and the cluster source fire simultaneously, potentially resulting in the placement of material as directed by the path of the beam. In the second embodiment, a two-stage process is employed, where a charge image is first patterned, and then subsequently developed by nanoclusters upon opening a high-speed shutter.

In this chapter, progress made toward realizing such a system will be discussed. Section 4.3 discusses some of the basic theory behind electrostatic patterning, while section 4.4 reports the initial experimental work thus far conducted.

4.3 Theory

Electric fields arising from the presence of charge stored in an electret drive any electrophotographic process. The horizontal and normal components of the electric field used to attract a charged particle are defined below. Reference for the below equations can be made to the schematic shown in Figure 80. Charged particles are attracted to a latent charge image by the Coulomb force $F$:
\[ F = QE \]  \hfill (1)

where \( Q \) is the charge of the particle and \( E \) is the electric field associated with the latent image. The electrostatic latent image on the surface of the electret is represented by a sinusoidal charge pattern given by:

\[ \sigma(y) = \sigma_0 + \sigma_k + \cos ky \]  \hfill (2)

where \( \sigma \) is the surface charge density, \( \sigma_0 \) is the amplitude of the nonvarying component, and \( \sigma_k \) is the amplitude of a spatially varying surface charge component, as illustrated in Figure 80. The line frequency \( k \) is equal to \( 2\pi / \lambda \), where \( \lambda \) is the period of the charge pattern. The normal component of the field above the image is given by

\[ E_z = \frac{\sigma_k \tanh kse^{-k(z-s)}}{\varepsilon_d \tanh ks + \varepsilon_s} \cos ky \]  \hfill (3)

where \( \varepsilon_s \) and \( \varepsilon_d \) are the permittivities of the electret layer and air, respectively, and \( s \) is the thickness of the electret. The horizontal component of the field is given by

\[ E_y = \frac{\sigma_k \tanh kse^{-k(z-s)}}{\varepsilon_d \tanh ks + \varepsilon_s} \sin ky \]  \hfill (4)

\[ \sigma(y) = \sigma_0 + \sigma_k + \cos ky \]

Air \( \varepsilon_d \)

Electret \( \varepsilon_s \)

\[ s \]

Figure 80: Dielectric slab model used in the calculation of electric fields in the region above the charge-patterned electret.
4.4 Experimental work

The first step toward realizing the vision of an in-situ electrophotographic machine was to establish that ionized, inorganic nanoclusters suspended in an Ar carrier gas could in fact develop latent charge images patterned by an electron or ion beam. In parallel, a variety of electrets were tested for their ability to store charge when exposed by an electron beam.

4.4.1 Electron beam charge-patterning of electrets

An electron beam was used to pattern charge into a variety of electrets: mylar, PMMA, polyimide, SiO₂ treated with HMDS, and spin-on glass (SOG). FEI Company's Environmental SEM Field Emission Gun (ESEM-FEG) XL-30 was used for pattern exposure. The software and hardware lithography package from JC Nabity was used to control the electron beam during patterning. PMMA films were prepared by spinning for 60 seconds at 6000 rpm, soft-baking at 90 °C for one hour, then hard-baking at 500 °C for one hour. Polyimide films were prepared by spinning for 40 seconds at 4000 rpm, soft-baking at 55 °C for 2 hours and hard-baking at 350 °C for 30 minutes. After patterning, toner particles dissolved in isoparaffin petroleum solvent (from Specialty Toner Corp.) were injected by pipette onto the surface of the substrate, thus developing the image. Excess toner was washed away by rinsing in isoparaffin petroleum.

The key parameters for charge patterning are the energy of the electrons and the dose. Higher energy electrons can damage the surface of certain electrets, as seen in Figures 81 - 82. Here, 30 keV electrons were used to pattern 100 µm squares in mylar. Patterns written at 5 kV do not exhibit the same type of surface defects as determined by optical microscopy. Accelerating voltages below 10 kV were utilized for all experiments to minimize surface damage.
Figure 81: Optical image of a mylar surface after exposure to 30 keV electrons. The features shown are ~100 μm squares.

Figure 82: Optical image of one of the 100 μm squares shown in Figure 81.

Charge patterns have been successfully developed with toner at these lower electron energies for most of the materials tested. Table 6 summarizes the results obtained after testing the charge storage abilities of the listed electrets.

Table 6: Comparison of the approximate dose required to store charge patterns in electrets, and the subsequent best resolution achieved after development.

<table>
<thead>
<tr>
<th>Electret</th>
<th>Dose (μC/cm²)</th>
<th>Best Resolution After Development</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ treated with HMDS</td>
<td>1,000-100,000</td>
<td>5 μm</td>
</tr>
<tr>
<td>PMMA</td>
<td>1,000-50,000</td>
<td>N/A</td>
</tr>
<tr>
<td>Polyimide</td>
<td>500-8000</td>
<td>500 nm</td>
</tr>
<tr>
<td>SOG</td>
<td>100-1000</td>
<td>N/A</td>
</tr>
<tr>
<td>Mylar</td>
<td>1-10</td>
<td>800 nm</td>
</tr>
</tbody>
</table>

To ensure that pattern formation was achieved due to electrostatic forces as opposed to particles settling into regions damaged by the electron beam, developed areas were washed with solvent to remove the toner particles and then discharged with isopropyl alcohol (IPA). Once discharged, the electrified patterns could no longer be developed by toner, and were also no longer visible by SEM. In contrast, when not washed in IPA, charge patterns could be repeatedly rinsed with solvent and re-developed with toner to expose the latent image.
The electret requiring the least amount of charge to obtain a voltage contrast image by SEM, and also to develop successfully in toner, was mylar. Using doses of 1 to 10 \(\mu\)C/cm\(^2\) and electron energies of 5 keV, negatively electrified patterns have been written, as seen in Figure 83. An image of the electrified pattern after development in toner is shown in Figure 84. The developed patterns vary in toner density from feature to feature over a large area, as seen in Figure 84. Magnified images of two 100 \(\mu\)m squares showing variation in toner density are shown in Figure 85. The inconsistent density and poor features at the edges of the pattern are due largely to non-homogenous washing, which should not be an issue for use with inorganic nanoclusters, as no wash step is required.

**Figure 83:** SEM voltage contrast image of negatively electrified charge patterns.

**Figure 84:** Optical image at 5x of the patterns in Figure 83 after development with toner.

**Figure 85:** Optical image at 20x of two 100 \(\mu\)m squares of positive toner developed on mylar. Squares located on the fringes of the array (left) exhibit denser toner deposition on the edges, while squares located at the center of the array (right) have a more uniform deposition with cleaner edges.
The best linewidths achieved for mylar substrates after developing in toner were approximately 5 μm, as seen in Figure 86. Although smaller structures below one micron were observed, typically the edges were extremely rough and poorly defined. This effect is due in part to the wash, but also to the size of the toner particles used, which were on the order of 100 nm in diameter. Thus, any lines observed below approximately 1 μm were typically loosely packed and irregular.

The material that showed the most consistency in results was polyimide. Although mylar could be patterned at lower doses, higher resolution features could be achieved with greater regularity on polyimide. Figure 87 shows an SEM image of toner particles developed on polyimide.
Figure 87: SEM image of toner particles on polyimide. Courtesy of Jon Varsanik.

SiO₂ and SOG were poor electrets for patterning charge by SEM, as SiO₂ required doses in the mC/cm² range, while SOG was damaged even by low energy electrons. Ultimately, the best materials tested for patterning charge by SEM were mylar and polyimide.

4.4.2 Developing charge patterns with inorganic nanoclusters

The first set of experiments conducted to see if particles generated by the Nanocluster Source could be attracted to an electrified image involved inserting a charge patterned substrate into the 6-way deposition chamber shown in Figure 88. Substrates were placed in areas A and B, as indicated in the schematic, where region A was completely out of the beam path, while region B was directly incident to the beam. For such experiments, no deposited Cu clusters could be detected anywhere on substrates placed at A for deposition times up to several hours, while substrates placed at B showed uniform cluster coverage without any selective deposition on the charge patterns.
To test the ionization of the nanoclusters, an electrode was placed at A and held at a potential of +80V relative to the rest of the chamber and casing, which was grounded. Cluster deposition commenced for times up to 30 minutes, at which point the electrode was removed from vacuum and examined. A coating of material could be observed on the electrode, indicating that clusters had in fact been deposited. Similar results were achieved for electrodes placed at B, and also for electrodes held at -80V. Smaller amounts of deposition were noticed for electrodes held at -80V, indicating that the Cu cluster mixture contained a smaller proportion of positively charged clusters, which are the variety of interest for developing a negative charge pattern, than negatively charged clusters.

Significantly, although no Cu clusters were observed on substrates positioned at A after depositing for varying amounts of time, these substrates no longer developed toner once removed from the vacuum. This suggests that somehow the electrified pattern was discharged at some point during the deposition. Substrates placed at A and subjected to vacuum, and also to Ar flow, still developed toner once removed from vacuum; however, even brief exposure to the cluster source once a plasma had been struck would immediately neutralize the charge pattern without depositing any Cu clusters. Thus, it is hypothesized that charged species from the Ar plasma were in fact discharging the electrified pattern upon raising the gate valve. Haberland has observed the presence of
Ar in deposited films for samples floated at high negative potentials, indicating that Ar\(^+\) ions can in fact be pulled from the plasma in the presence of an electric field. Given this result, methods for the filtration of charged species, specifically by mass, were explored. A mass quadrupole capable of filtering particles by size was obtained to select only the desired nanoclusters from the beam of material emerging from the Nanocluster Source, thus eliminating the presence of any unwanted ions. Experiments utilizing this quadrupole in concert with the Nanocluster Source are currently being conducted.
5 Conclusions and Future Work

Two modes of energetic beam-mediated fabrication have been investigated, namely FIB direct-writing of nanoparticles and nanoxerography. It has been demonstrated that Ag-capped nanoparticles can be patterned by a FIB with resolutions of 100 nm at speeds vastly surpassing those of any electron beam direct-write method to date. Also, rudimentary three-dimensional structures have been fabricated with a resistivity of $15.3 \pm 1.9 \, \mu \Omega \cdot \text{cm}$, a value within one order of magnitude of bulk Ag. Methods for building structures in-situ by delivering nanoparticles directly to the site of fabrication have been proposed, along with a technique for fabricating unsupported structures. Additionally, a new unit of merit for characterizing direct-write processes, termed resistivity-dose ($\mu \Omega \cdot \mu \text{C/cm}$), has been introduced. In regard to nanoxerography, a source capable of delivering inorganic nanoclusters in a carrier gas of Ar has been characterized. A relationship between magnetron power and nanocluster size has been determined, and the use of such clusters for the development of latent charge images is currently being investigated. Various electret materials to be used in the nanoxerography process have been studied, with mylar and polyimide being the two most promising candidates. Though progress has been made in advancing these two modes of fabrication, significant work remains to be done. This chapter will propose some areas of future work for both techniques.

Although FIB direct-writing of nanoparticles has been demonstrated to be a promising technique for fabricating nanostructures, the problem of structure lift-off and conductivity still demands greater scrutiny. An ideal experiment to attempt would be to expose nanoparticles with higher energy Ga$^+$ ions, or perhaps even a beam of lighter ions, to increase the penetration depth and thus facilitate the patterning of thicker layers of resist. Doing so could allow for the fabrication of higher conductivity structures without relying on the stacking methods currently used for 30 keV Ga$^+$ ions. Given these limitations, however, the methods for building structures in three dimensions require significant improvement, particularly in the area of alignment. The use of a more accurate stage, such as a laser interferometer stage, could improve results, and also more clever designs employing multiple fiducials could increase alignment accuracy. Perhaps the best solution to the alignment problem is, of course, the development of a
reliable in-situ process. As has been a theme for this entire thesis, the vision of a single pump-down machine remains the most elegant solution to problems pertaining not only to the techniques proposed here, but also to issues in the realm of general fabrication.

Work on nanoxerography is still in its early stages, and requires much greater investigation. With the use of the mass quadrupole, unwanted charge species such as Ar$^+$ ions or any other ions from the plasma can be filtered, thus leaving only clusters of the desired size and charge. Use of this mass filter should hopefully solve the problem of pattern discharge currently observed. If in fact inorganic nanoclusters can be used to develop these latent charge images, combining the Nanocluster Source with an energetic beam source such as an electron beam or ion beam becomes readily viable.

Further characterization of nanoclusters generated from the Nanocluster Source is also necessary. Though it seems obvious that structures fabricated from such clusters would be more conductive than their organometallic counterparts, controlled experiments must be conducted to verify this conjecture.

Finally, although much work remains in the study of both fabrication techniques, promise has been shown particularly in the case of FIB direct-write that such a method could be competitive with standard chip and mask repair technologies such as FIB CVD. Dedicated future work on nanoxerography should realize its potential as a novel technique for the rapid in-situ fabrication of nanostructures.
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