NANOPANTOGRAPHY WITH REMOVABLE MEMBRANE-BASED ELECTROSTATIC LENS ARRAYS

by Ryan Sawadichai

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Chair of Committee: Vincent M. Donnelly

Co-Chair of Committee: Demetre J. Economou

Committee Member: Michael Nikolaou

Committee Member: Paul Ruchhoeft

Committee Member: Jiming Bao

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Dedicated to my wife, Shinhoo, my parents, and my grandparents.

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Abstract

Nanopantography is a method for massively parallel writing of nano-sized patterns using an ion beam. In this process, a broad area, collimated, nearly-monoenergetic ion beam is directed towards an array of micron-scale electrostatic lenses in direct contact with a substrate. By applying an appropriate DC voltage to the lens array with respect to the substrate, the ion beamlet entering each lens converges to a fine spot that can be 100 times smaller than the diameter of each lens. Previously, lenses fabricated directly on the silicon substrate were used to etch 3 nm diameter holes in silicon by exposure to a monoenergetic Ar^+ ion beam and chlorine gas.

This work reports on the development of removable and reusable free-standing membrane-based electrostatic lens arrays that are designed to pattern any conducting surface. The lens arrays are fabricated on a silicon wafer coated with PMGI, SU-8, gold, copper, and PMMA. Lens openings are lithographically defined, and an acrylic frame is placed over the array. The lens patterns are etched through the SU-8 and the membrane is released by dissolution of the PMGI layer. The applied voltage used to focus the ion beamlets also serves to electrostatically clamp the lens array to a conducting substrate, which is observed as a flattening of the membrane against the substrate surface and an increasing capacitance measured between the lens array and the substrate. An array with lens diameters between 0.8 μ m and 1.5 μ m was used to pattern features as small as 20 nm on a silicon substrate using a 70 eV Ar⁺ ion beam.

to the variation of lens potential, lens aspect ratio, and lens size. Simulations for this lens geometry agreed with the experimentally observed results when chromatic and spherical aberrations are considered. Based on the simulation results, it should be possible to print much smaller features via a step and repeat process with a thinner dielectric and narrow lens diameter. Diagnostics of a positive ion beam extracted from a pulsed oxygen plasma were conducted, confirming that the majority of the beam consists of 100 eV O_2^+ ions. Patterning of graphene with the nanopantography method was conducted with the O_2^+ ion beam, resulting in defect production in a focused spot 17 times smaller than the lens openings.

Dedicati	on•••••••iii
Acknow	ledgments ······ iv
Abstract	t •••••• vi
Table of	Contents······viii
List of T	'ables ······ xi
List of F	igures ······xii
Chapter	1 Introduction ······ 1
1.1.	The Importance of Sub-10 nm Patterning 1
1.2.	The State of Sub-10 nm Patterning 2
1.3.	Nanopantography ····· 4
1.3.	1. The Principle of Nanopantography 4
1.3.2	2. Previous Work in Nanopantography 5
1.3.	3. Motivation for Print and Repeat Nanopantography 6
1.4.	Research Goal 8
1.5.	Organization of Dissertation
Chapter	2 Literature Review
2.1.	Current Methods for Sub-10 nm Patterning10
2.2.	Low Energy Broad Ion Beam Sources and Applications15
2.3.	Previous Work in Nanopantography22
2.4.	Patterning of Graphene ·····27
Chapter	3 Methods
3.1.	Experimental apparatus
3.1.1.	Generation of a nearly monoenergetic Ar ⁺ ion beam
3.2. Analyz	Measurement of Ion Energy Distribution Using a Retarding Field Energy zer
Chapter Electros	4 Print and Repeat Nanopantography with Removable, Reusable tatic Lens Arrays40
4.1.	Removable Lens Development
4.1.	1. Material Considerations
4.1.2	2. Fabrication Overview

Table of Contents

4.1.	3.	Lens Clamping ······44
4.1.	4.	Clamped Lens Release
4.2.	Exp	erimental Etching Results
4.2.	1.	Proof of Concept Experiment
4.2.	2.	Effect of Lens Geometry
4.3.	Sun	nmary
Chapter	· 5	SIMION Simulations of Nanopantography Lens Focusing68
5.1.	Met	hods
5.1.	1.	Macroscopic Domain: Analytical Solution70
5.1.	2.	SIMION Simulation Domain75
5.2.	Sim	ulation Results
5.2.	1.	Overview of Aberrations
5.2.	2.	Effect of System Geometry
5.2.	3.	Effect of Lens Geometry
5.2.	4.	Lens Scaling91
5.3.	Mod	del Limitations ······94
5.3.	1.	Ion Angular Distribution94
5.3.	2.	Contrast and Real Feature Sizes
5.4.	Sun	1 mary
Chapter	· 6	Patterning of Carbon-Based Materials with an Oxygen Ion Beam 100
6.1.	Oxy	gen Beam Diagnostics
6.1.	1.	Experimental Methods for Oxygen Ion Beam Diagnostics 102
6.1.2. Determination of Oxygen Ion Beam Composition via Time-of-Flight Mass Spectrometry		
6.1.	3.	Effect of Pressure 110
6.1.	4.	Effect of Bias Delay 113
6.2.	Patt	erning of PMMA with an O_2^+ Ion Beam 117
6.3.	Patt	erning of Carbon and Graphene with an O_2^+ Ion Beam $\cdots 120$
6.4.	Sun	nmary
Chapter	• 7	Conclusions and Recommendations 130
7.1.	Con	clusions ······ 130

References ······ 13			137
7.2.	Reco	ommendations for Future Work	133
7.1.	3.	Graphene Patterning	132
7.1.	2.	Lens Simulations	132
7.1.	1.	Print and Repeat Nanopantography	131

List of Tables

- Table 6.1: Summary of experimental conditions and measured feature sizes for O_2^+ beam patterns formed in PMMA using a metal mesh with 100 µm diameter holes as the lens. 119

List of Figures

Figure 1.1: The smallest computer devices over time. The image corresponding for 2020 shows an experimental class of mm-scale sensors known as "motes" or "smart dust," which can form wireless sensing and computing networks. [7]
Figure 1.2: (left) Side view of an array of electrostatic lenses focusing a broad area collimated ion beam to a single spot. (right) Demonstration of sample stage tilting to write arbitrary patterns
Figure 1.3: SEM images of 7 nm trench, 13 nm UH logo, and 3 nm hole patterned via nanopantography followed by highly selective Cl ₂ plasma etching
Figure 1.4: SEM images of 10 nm Ni nanodot deposition from Xu et al. [27] 6
Figure 1.5: Schematic of print-and-repeat nanopantography with a reusable and removable lens array
Figure 2.1: The widening gap between wavelength of light source used in lithography and feature resolution
Figure 2.2: Schematic of SAQP. Sidewalls are deposited on a mandrel, etched to expose the mandrel, and the mandrel is removed, leaving the sidewalls as a new mandrel. The process is repeated in SAQP. From Nakayama et al. [33]
Figure 2.3: Energy regimes in ALE, from Kanarik et al. [48] In Regime 1, energy is too low to completely remove one monolayer. In Regime 3, energy is high enough to cause physical sputtering, removing more than one layer
Figure 2.4: SEM images of 20° (left) and 10° (right) blazed gratings etched with a reactive ion beam. Reproduced from Liu et al. [50]
Figure 2.5: The original Kaufman ion source, one of the most common broad beam ion sources, from Kaufman et al. [61] Two grids are used: the screen grid confines electrons to the source while the second grid accelerates ions
Figure 2.6: Schematic of CCP broad beam ion sourced used by Lossy and Engemann [65]
Figure 2.7: Schematic of self-neutralization mechanism in a nearly-monoenergetic positive ion beam extracted from the afterglow of a pulsed plasma. Reprinted from Chen et al. [77]

Figure 2.8: SEM images of 1.3 μm diameter holes etched with a 75 μm opening metal mesh. The substrate was exposed to 200 eV ions with 188.9 V bias on the lens electrode for 4 hours. From Xu et al. [26]
Figure 2.9: SEM images of 10 nm and 20 nm diameter holes etched with a 950 μm opening lens array fabricated on Si. The substrate was exposed to 200 eV ions with 188.9 V bias on the lens electrode for 4 hours. From Xu et al. [26]
Figure 2.10: (a) SEM image of feature formed by nanopantography followed by highly selective anisotropic etching versus (b) TEM image of feature formed by single-step nanopantography. Reprinted from Tian [80]
Figure 2.11: (a) Schematic of microlens array focusing of charged nanoparticle aerosol jets. (b) and (c) bent nanopillar structures obtained by translation of the sample stage. Adapted from Jung et al. [83]
Figure 2.12: ALE of graphene from Yeom et al. [121] Top layer of graphene is modified by O ₂ /O radicals (a), chamber is evacuated (b), graphene is exposed to 30 eV Ar neutral beam (c), single layer of graphene is removed (d)
Figure 3.1: Schematic of nanopantography experimental apparatus
Figure 3.2: Drawing of the ICP source. [80]
Figure 3.3: Schematic of the pulsed plasma power and bias sequences for Si etching experiments with an Ar ⁺ ion beam
Figure 3.4: Schematic of system setup for ion energy distribution measurement. The sample stage is not shown but was present in the sample processing between the RFEA and source
 Figure 3.4: Schematic of system setup for ion energy distribution measurement. The sample stage is not shown but was present in the sample processing between the RFEA and source
 Figure 3.4: Schematic of system setup for ion energy distribution measurement. The sample stage is not shown but was present in the sample processing between the RFEA and source
 Figure 3.4: Schematic of system setup for ion energy distribution measurement. The sample stage is not shown but was present in the sample processing between the RFEA and source

- Figure 5.4: Focusing curves for 1 µm lenses and 70 eV ions with FWHM of the IED varying from 0 (monoenergetic ions) to 9 eV. The yellow region highlights the range where feature size is within 20% of the optimum feature size at 3 eV FWHM.

Figure 5.5: Percentage of ions that can pass through the lens and reach the substrate surface versus focusing voltage for a 70 eV Ar⁺ ion beam with 3 eV FWHM. Figure 5.6: Expected feature size vs. focusing voltage for varying source-to-mesh Figure 5.7: Expected feature size vs. focusing voltage for varying mesh-to-lens Figure 5.9: SIMION simulations showing expected feature size vs. focusing voltage for various dielectric thickness (lens length) to lens diameter ratios for 1 µm thick Figure 5.10: Simulation of 1:1 dielectric thickness to diameter ratio (left) and 2.5:1 (right) for 100 nm and 1 µm dielectric thickness with varying focusing voltage. Ar⁺ ion beam had 70 eV peak ion energy, 3.5 eV FWHM.......92 Figure 5.11: SEM cross sections of 3 nm holes in silicon with SiO_2 lenses on Si (230) nm diameter, 300 nm dielectric thickness) before (left) and after (right) highly Figure 5.12: 1 µm lens with 70 eV Ar⁺ ions at 65-72 V lens potential with shapes of ion radial position distribution at the substrate surface in red and Gaussian fit shown Figure 5.13: FWHM of the ion position distribution (black squares), percent of ions falling within the FWHM, and the slope of the distribution at the FWHM position Figure 6.1: Schematic of the pulsed plasma power and bias sequences for oxygen beam Figure 6.2: Time-resolved ion current for a 96.8 eV peak energy, 6.8 eV FWHM Ar⁺ ion beam generated by applying +98.2 V, 15 µs synchronous boundary bias 20 µs into the afterglow of a 10 kHz, 20% duty cycle pulsed plasma...... 105 Figure 6.3: Ion energy distribution for an ion beam generated from pure O₂ plasma at 800 W, 65% duty cycle, and +98.2 V boundary bias applied 15 µs after plasma is Figure 6.4: Time-resolved ion current for a 95.5 eV peak energy, 6.4 eV FWHM O_2^+ ion beam generated by applying +98.2 V, 15 µs synchronous boundary bias 15 µs

into the afterglow of a 10 kHz, 65% duty cycle pulsed O₂ plasma...... 108

Figure 6.5: Ion energy distributions measured with the I	RFEA under different pressures
(8 - 20 mTorr) of the ICP source. Otherwise, base	e conditions defined in Section
6.1.1 were used	

Figure 6.7: Ion energy and FWHM measured with the RFEA	A with different bias delays
applied $1 - 20 \mu s$ after plasma-off (corresponding to 66	$-85 \ \mu s$ in the cycle). Bias
duration remained fixed at 15 µs	

- Figure 6.8: Optical microscope images of O_2^+ beam patterns formed in PMMA at various focusing voltages and etching times. A metal mesh with 100 μ m diameter holes was used as the lens. 118

Chapter 1 Introduction

1.1. The Importance of Sub-10 nm Patterning

Since the invention of the first metal oxide field effect transistor (MOSFET) at Bell Laboratories in 1959, the main method of technological progress in the semiconductor industry has been decreasing the size of devices to fit a higher density of devices in a product [1-3]. Not only has this trend shrunk the size of computers from entire rooms to fitting inside a pocket (Figure 1.1), but it has enabled the technologies essential to the modern world such as personal computers, the internet, mobile devices, wireless communications, cloud computing, and artificial intelligence. By reducing the physical dimensions of semiconductor devices, the resulting improvements in information processing speed, number of computations per computing cycle, information storage density, and power consumption have been fundamental in creating smaller computers and new electronic devices. Semiconductor devices have been employing transistors with feature definition in the sub-10 nm scale since the 22 nm logic node debuted in 2012 [4-6]. Additionally, there are numerous devices in the research stage that require nanoscale feature definition such as nanofluidic biomolecule sensors and separators, and smart dust.



Figure 1.1: The smallest computer devices over time. The image corresponding for 2020 shows an experimental class of mm-scale sensors known as "motes" or "smart dust," which can form wireless sensing and computing networks. [7]

1.2. The State of Sub-10 nm Patterning

Photolithography has been the primary method for patterning microelectronic devices for decades [8]. The main light source in optical lithography is the 193 nm deep ultraviolet ArF excimer laser, which has been in use from 2003 to the present day due to the significant ingenuity that has been employed to extend optical lithography beyond its predicted limits [9]. However, relying on 193 nm wavelength light to pattern sub-10

nm features requires multiple exposures and additional processing steps, which adds significant cost and reduces yield and throughput compared to single exposure processing.

Various alternative technologies have been explored to replace multipleexposure optical lithography [9]. Extreme ultraviolet (EUV) lithography is the leading technology for sub-10 nm patterning in industry, but the added complexity of EUV systems has delayed its introduction into high-volume manufacturing until 2018 and the nine-figure price tag of each EUV tool makes them prohibitive for laboratory-scale and niche devices [10–12]. Block copolymer directed self-assembly can only produce a limited subset of patterns with dimensions < 10 nm [13–16], but is still actively researched by academic institutions and for high volume manufacturing [9]. Nanoimprint lithography has shown potential for high throughput and low cost patterning on the sub-10 nm scale but is limited by defects, air bubble trapping, template contamination, and adhesion [17–20]. Electron beam [21,22] and scanning probe lithographies [23] have long been able to achieve sub-10 nm resolution and are widely used in making photolithography masks, but are not used in industry to directly pattern wafers due to low throughput even with multiple beams in parallel [24,25]. Many other creative techniques have demonstrated sub-10 nm resolution in research settings as well; this report will focus on a high-throughput and low-cost technique developed by researchers at the University of Houston called nanopantography [26].

1.3. Nanopantography

1.3.1. The Principle of Nanopantography

Nanopantography is a method for massively parallel patterning of nanoscale features over broad areas using an ion beam [26–28]. In this process, a broad area, collimated, nearly-monoenergetic ion beam is directed towards an array of micron-scale electrostatic lenses in direct contact with a substrate. Lenses can be fabricated directly on a substrate as shown in previous studies (Figure 1.2) or they can be made into removable and reusable structures. By applying an appropriate DC voltage between the substrate and the top electrode of the lens array, ion beamlets are focused on the Si substrates into spots that have been demonstrated to be up to 100 times smaller than the opening diameter of the lenses [27–29]. The stage holding the substrate can be tilted to laterally translate the focal point at the bottom of each lens, allowing for the writing of arbitrary patterns on the substrate.



Figure 1.2: (left) Side view of an array of electrostatic lenses focusing a broad area collimated ion beam to a single spot. (right) Demonstration of sample stage tilting to write arbitrary patterns.

1.3.2. Previous Work in Nanopantography

Nanopantography has been demonstrated by Tian to pattern sub-10 nm features such as the etched holes and trenches shown in Figure 1.3. Complex shapes have also been constructed using an improved two-step process involving the etching of native oxide through nanopantography followed by highly selective chlorine plasma etching under photo-assisted etching (PAE) conditions, shortening the time needed for the nanopantography step and improving both throughput and resolution [28,29]. Deposition of Ni nanodots was also demonstrated by Xu as shown in Figure 1.4.



Figure 1.3: SEM images of 7 nm trench, 13 nm UH logo, and 3 nm hole patterned via nanopantography followed by highly selective Cl₂ plasma etching.



10 nm Ni dot deposition

Figure 1.4: SEM images of 10 nm Ni nanodot deposition from Xu et al. [27]

1.3.3. Motivation for Print and Repeat Nanopantography

Developing removable lens arrays is a key requirement for extending nanopantography to industrial scale processes. The present methods of nanopantography requires electrostatic lenses to be fabricated onto the surface of a substrate, adding complexity and limiting the variety of compatible substrates. The lenses are also restricted to etching in the locations on which they are fabricated, requiring new lenses to be fabricated if patterning is desired in a different location or in a later process step. The lenses might need to be removed through plasma etching in a real microelectronics fabrication process, increasing the risk of damage to the substrate. Removable lens arrays solve these problems by allowing easy removal and repositioning of the lens array, reducing the complexity and cost of integrating nanopantography into a fabrication process. In this investigation, removable and reusable free-standing membrane-based electrostatic lens arrays were developed. In this new method of print-and-repeat nanopantography, the lens array is placed, rather than fabricated, on top of the substrate (Figure 1.5). The applied voltage used to focus the ion beamlets in conventional nanopantography also serves to electrostatically clamp the lens array to a conducting substrate in print-and-repeat nanopantography, which is observed as a flattening of the membrane against the substrate surface and an increasing capacitance measured between the lens array and the substrate. In addition to increasing throughput, this print-and-repeat method of nanopantography will also be extended to pattern graphene on silicon with the potential to pattern any conducting substrate.



Figure 1.5: Schematic of print-and-repeat nanopantography with a reusable and removable lens array

1.4. Research Goal

The goal of this research is to demonstrate print-and-repeat nanopantography to pattern a variety of substrates such as silicon and graphene. In addition, the factors affecting focusing of ion lenses will be studied via SIMION simulation to fabricate scaled and optimized lenses and push resolution limit of nanopantography to 1 nm.

1.5. Organization of Dissertation

Chapter 2 is a comprehensive literature review of topics related to recent development of lithography, including challenges in sub-10 nm patterning, ion beam sources, control of ion energy distributions and generation of a nearly monoenergetic ion beam from a pulsed plasma, space charge effect and compensation, and previous work by nanopantography.

Chapter 3 discusses the details of the apparatus, pulsed power methodology used for generation of a self-neutralized ion beam, and a retarding field energy analyzer used to perform plasma diagnostics.

Chapter 4 discusses the development of freestanding removable and reusable electrostatic lens arrays and their use to pattern silicon substrates with an argon ion beam in a background of chlorine gas.

Chapter 5 presents simulations of lens array focusing under various lens geometries and ion beam assumptions to gain insight into optimal operating conditions and resolution limits of nanopantography. Chapter 6 presents the results ion beam diagnostics of an oxygen ion beam and its application to patterning carbon-based materials including photoresist and graphene using the nanopantography method.

Chapter 7 gives the conclusions of this work and recommendations for future work.

Chapter 2 Literature Review

This review begins with an overview of the current and previously considered methods for sub-10 nm patterning used in high-volume industrial production of semiconductors followed by a discussion of low energy broad beam ion sources with special consideration of the nearly-monoenergetic space charge self-neutralized source used in nanopantography. Previous work in patterning using the nanopantography method is reviewed followed by a discussion of graphene patterning.

2.1. Current Methods for Sub-10 nm Patterning

For decades, lithography and plasma etching have been the two techniques, when used together, that provide the throughput, resolution, and precision necessary for leading-edge high-volume microelectronics fabrication. While lithography has long been able to achieve sub-wavelength feature sizes (Figure 2.1) with the use of optical proximity correction, phase shift masks, off-axis illumination, immersion lithography, and double exposure [30], plasma etching has extended the use of the 193 nm ArF UV light source more than an extra decade from its introduction in the 90 nm logic node in 2003 to the present day through the method of spacer patterning [9,31]. An extension of spacer patterning, self-aligned quadruple patterning (SAQP), is the leading edge technique for 193 nm ArF immersion lithography and has been used in high-volume production to achieve feature sizes as small as 7 nm fins [6,32]. In this technique (shown schematically in Figure 2.2), only one lithography step is employed, followed by repeated plasma etching and chemical vapor deposition of sidewall spacers which

results in quadrupling of the pattern density originally defined lithographically. Precise control of plasma etch parameters is required, since final patterns can be sub-10 nm and six or more plasma etching steps are typically involved, including both anisotropic (Figure 2.2 (d), (f), (i), and (k)) and isotropic ((b) and (g)) etching.



Figure 2.1: The widening gap between wavelength of light source used in lithography and feature resolution.



Figure 2.2: Schematic of SAQP. Sidewalls are deposited on a mandrel, etched to expose the mandrel, and the mandrel is removed, leaving the sidewalls as a new mandrel. The process is repeated in SAQP. From Nakayama et al. [33]

While SAQP has allowed for the recent continuation of Moore's law, the method has reached limitations due to increasing precision requirements, complexity, cost, and shapes of patterns that are able to be created [34–36]. Multiple alternatives for sub-10 nm patterning have been developed, with their relevance to high-volume manufacturing summarized in

Table 2.1. Extreme ultraviolet lithography (EUV) is the clear path forward, and is the only method that provides the combination of precision, yield, throughput, and cost necessary for large-scale fabrication [9,12,34-36]. However, the capital cost for a single 13.5 nm EUV tool exceeds \$100 million and their use has been restricted to large industrial players with billions to invest in manufacturing facilities. Even in industry, EUV alternatives are still considered viable alternatives for specific patterns relevant to specialized applications. Nanoimprint lithography is a method involving physical contact between a template and resist and is already used actively in research [37,38]. Recently, nanoimprint lithography has been deployed by Kioxia to produce flash memory thanks to advancements in stepper systems increasing alignment and throughput, while mask life has increased to over 300 lots per mask and multiple beam lithography systems have reduced the time to make new and spare masks [39,40]. Directed self-assembly of block copolymers is still under consideration for specialized shapes such as nanowires for future nodes, but continued problems with pattern placement and defects have driven their recent focus towards unconventional electronics such as flexible devices [41]. Maskless lithography methods such as electron beam, ion beam, and dip-pen nanolithography are no longer under consideration for high-volume integrated circuit manufacturing [9], though multiple-beam methods remain relevant for improving throughput of mask writing for optical and EUV lithography [42–44].

Table 2.1: Summary of current and future patterning techniques considered for high-
volume manufacturing. Compiled and reproduced from 2017 and 2020
editions of the International Roadmap For Devices and Systems. [9,45]

Next Generation Technology	First Use in HVM	Feature Type	Device Type	Key Challenges	Required Date for Decision Making
Multiple Patterning Extension to >4X Patterning	2019	Vias, contacts or cut patterns for high performance logic	"7nm" Logic Node	-Tolerances, EPE and OL -Development cycle too long -Cost of process	Already Committed
EUV Single Patterning	2019	22 to 24 nm hp CH/Cut Levels Back end metals at 18 nm hp LS	"7nm" Logic Node	-Pellicles -Resist speed combined with LER and Stochastics -shot noise	Already Committed
EUV Multiple Patterning	2022	12nm hp LS	"3nm" Logic Node	-Tolerance, EPE, and Overlay	2021
EUV high NA	2025	10.5nm hp LS	"2.1nm" Logic Node	-Stitching of two mask patterns -Shot noise	2024
EUV new wavelength	2028 ?	8nm hp LS ?	"1.5nm" Logic Node	-EUV source power -Resist material -Actinic blank and patterned mask inspection	2030
Nanoimprint	2019	20nm lines and spaces 20 to 30nm contact holes	3D Flash Memory	-Defectivity -Overlay -Master Template fabrication and inspection <20nm -Defect repair -Mass-production capacity	Product Evaluation Completed
DSA (for pitch multiplication)	2022	Contact holes/cut levels for logic Possibly nanowire patterning	"3nm" Logic Node	-Pattern placement -Defectivity and defect inspection -Design -3D Metrology	2021
Maskless Lithography (ML)	No current leading edge semiconductor plants	Not applicable	Not applicable	-Concept demonstration -Functioning tool	Not applicable

2.2. Low Energy Broad Ion Beam Sources and Applications

While high energy (>10 keV) focused ion and electron beam sources are useful for creating patterns, several applications require low energy (tens to hundreds of eV) broad area ion beam sources. For example, atomic layer etching (ALE) employs a low energy ion beam to selectively remove a monolayer of a chemically modified surface [46–48]. The beam energy must be low enough to prevent physical sputtering of any underlying material, but also high enough to facilitate the complete conversion of one monolayer of the target surface to volatile products (Figure 2.3). Reactive ion beam etching (RIBE) is a technique where a substrate is etched by exposure to a source of reactive ions that are accelerated towards a substrate, typically with tens or hundreds of eV. RIBE has applications in optoelectronics and photonics, where it may be necessary to etch surfaces tilted with respect to a normal [49,50], etch smooth surfaces on III/V and II/VI semiconductors and other materials that cannot be achieved with plasma etching [51,52], or smoothen surfaces [53,54]. More recently, broad ion beam sources with 1 - 10 keV energy have been used for 3D imaging of materials through sectionby-section milling coupled with imaging in a scanning electron microscope [55–58]. Compared to higher energy focused ion beam systems, the relatively lower energies result in less substrate damage, less ion implantation into the substrate, and prevention of unwanted phase transitions while imaging a sample [55,58].



Figure 2.3: Energy regimes in ALE, from Kanarik et al. [48] In Regime 1, energy is too low to completely remove one monolayer. In Regime 3, energy is high enough to cause physical sputtering, removing more than one layer.



Figure 2.4: SEM images of 20° (left) and 10° (right) blazed gratings etched with a reactive ion beam. Reproduced from Liu et al. [50]

Kaufman, Harper, and Cuomo have published many of reviews of early broadbeam ion sources [59–63]. Early ion sources typically consisted of a dc plasma generated from a hot filament with magnetic confinement to enhance ion current and control beam shape and uniformity. One or more aligned grids are placed at the exit of the source to extract and accelerate ions to form a beam. In any gridded ion source, the extracted ion beam current is space-charge limited and given by the Child-Langmuir law as

$$j = \frac{4}{9} \epsilon_0 \sqrt{\frac{2eQ}{m} \frac{V^{3/2}}{d^2}}$$
(2.1)

where ϵ_0 is the permittivity of free space, *e* is the elementary charge, *Q* is the charge state of the ion, *m* is the mass of the ion, *V* is the extraction voltage, and *d* is the distance over which the extraction voltage is applied. In multi-grid systems (Figure 2.5), *V* is the potential difference between the first and second grids and *d* is the spacing between the accelerator grid and the preceding grid. In single-grid systems, *V* is given by the plasma potential with respect to the grid and *d* is given by the sheath thickness. To achieve ion current density greater than 1 mA/cm² for high ion current applications, large acceleration voltages must be applied, resulting in ion energies on the order of keV and excessive grid sputtering, increasing contamination and maintenance requirements. Multi-grid sources are typically used over a single-grid source for high current or high ion energy applications since the first grid experiences a smaller bias relative to the plasma and subsequent grids have aligned openings, minimizing sputtering [60,61]. Gridless ion sources have been developed using magnetic fields to create an electric field accelerate ions instead of biased grids, resulting in high ion current densities at relatively low ion energy such as in the end-Hall ion source invented by Kaufman, which achieved 4 mA/cm^2 of ion current with 30 eV Ar⁺ ions [64].



Figure 2.5: The original Kaufman ion source, one of the most common broad beam ion sources, from Kaufman et al. [61] Two grids are used: the screen grid confines electrons to the source while the second grid accelerates ions.

For ion assisted etching applications, ion current on the order of 0.1 mA/cm^2 is sufficient, allowing for the widespread use of single-gridded sources [59]. Harper et al. compared the performance of single-grid sources to dual-grid sources and found that single-grid sources supply more ion current at low (<200 eV) ion energy since the sheath thickness could be an order of magnitude smaller than the typical grid spacing of ~1 mm in dual-grid systems [59]. Interest in using reactive ion sources also led to the development of radio frequency (rf) and microwave plasma ion sources, since reactive plasmas accelerate the degradation of hot filament ion sources through corrosion of the filament in gases containing oxygen, fluorine, and chlorine and deposition of dielectric films from polymerizing plasmas [63,65]. A review of these sources has been published by Brown [66].



Figure 2.6: Schematic of CCP broad beam ion sourced used by Lossy and Engemann [65].

Lossy and Engemann describe one of the first capacitively coupled plasma (CCP) broad beam ion sources for materials processing with reactive gases [65]. The source geometry, shown in Figure 2.6, consisted of two cylindrically symmetric parallel electrodes operated at 27.12 MHz with the lower electrode also serving as one of the three ion extraction grids. Magnetic confinement was used to enhance plasma density. The second grid was negatively biased to accelerate electrons and the third grid was grounded. A maximum of 2 mA/cm² over a diameter of 2 inches was achieved with an O_2 plasma operated at 500 W. A Gaussian beam profile with beam divergence angle of

2.3° was measured. The source was characterized with a Langmuir probe at 100 W operation, yielding an electron temperature and plasma density of 10 eV and 2.6×10^{11} cm⁻³ near the center of the reactor and 3 eV and 6×10^{10} cm⁻³ 7 mm above the 1st grid. The plasma potential was found to be nearly independent of the extraction voltage applied on the 2nd grid. Ion energy distributions were measured with a retarding field energy analyzer and the energy spread was found to be 10% of the ion energy.

After extraction, the ion beam contains a net positive space charge that will lead to beam expansion and nearly complete loss of ion current density as the beam transits. Electron-emitting hot filaments are typically placed downstream of the ion extraction optics, providing a source of electrons that are attracted to the ion beam, neutralizing the space charge. Despite their widespread use, hot thermionic emission filaments need to be replaced frequently, lasting only tens to a few hundred hours [60]. Another approach long-studied in the field of space propulsion is the use of a secondary plasma to neutralize the ion beam, generated via hollow cathode or rf plasma [60,67–70].

Xu et al. [71] developed an Ar⁺ ion beam source generated from a pulsed rf plasma with a grid at the exit of the source to confine the plasma inside the source. A synchronous positive dc bias was applied in the afterglow to a boundary electrode immersed in the plasma. The source was capable of producing a nearly monoenergetic ion beam with FWHM less than 2% of the peak ion energy. Nam conducted simulations on the CCP source [72] and Shin et al. [73,74] conducted studies on a pulsed ICP with synchronous dc bias ion source and showed that T_e drops to zero over 10-20 microseconds in the afterglow. Since the ion energy spread scales with T_e , [75,76] and
applying a bias to a plasma raises the sheath potential to the applied bias plus ~4.8 T_e , a nearly monoenergetic ion beam can be extracted by application of synchronous dc bias in the afterglow of a pulsed plasma. Further studies by Chen et al. [77] showed that ions and electrons are able to escape the source during the early afterglow of a pulsed Ar⁺ ICP, forming a background plasma in the near-downstream region that provides a source of electrons to neutralize the transiting beam. A schematic of this mechanism is shown in Figure 2.7, with further explanation provided in Chen's dissertation [78].



Figure 2.7: Schematic of self-neutralization mechanism in a nearly-monoenergetic positive ion beam extracted from the afterglow of a pulsed plasma. Reprinted from Chen et al. [77]

2.3. Previous Work in Nanopantography

Nanopantography was first reported in 2005 by Xu et al to etch micro and nanopatterns in silicon using an Ar⁺ ion beam with the substrate exposed to a background of Cl₂ gas [26]. In the micropattern experiment (Figure 2.12), 1.3 μ m (as measured by SEM) diameter holes were etched in silicon using a metal mesh with 75 μ m diameter openings separated from the sample by a 100 μ m dielectric spacer. AFM scans of the holes showed that the bright white area formed the base of the hole, giving an opening diameter of 2.8 µm near the top and a FWHM of 1.2 µm which indicates that the SEM may be a measure of the FWHM rather than the opening size. The lens opening was reduced by ~60x according to the SEM measurements and ~25x according to the opening width measured by AFM. A large 6-point star region approximately 12 µm in diameter is also visible in SEM, though AFM measurements of the topography of this region were not provided. The outline of the lens most likely results from modification of the Si surface by fast neutral species generated from the beam or ultraviolet light emitted from the plasma. The 6-point star region may be caused by the extended exposure time of 4 hours to poorly focused ions with energy higher and lower than the ion energy distribution peak and this region should be less apparent with shorter exposure times or lens geometries that minimize these chromatic aberrations.



Figure 2.8: SEM images of 1.3 μm diameter holes etched with a 75 μm opening metal mesh. The substrate was exposed to 200 eV ions with 188.9 V bias on the lens electrode for 4 hours. From Xu et al. [26]



Figure 2.9: SEM images of 10 nm and 20 nm diameter holes etched with a 950 μm opening lens array fabricated on Si. The substrate was exposed to 200 eV ions with 188.9 V bias on the lens electrode for 4 hours. From Xu et al. [26]

Further experiments were reported in the same work demonstrating 10 nm diameter holes etched with a 950 nm diameter lenses fabricated on silicon with 50 nm Cr electrode layer thickness and 1000 nm SiO₂ dielectric thickness, resulting in a remarkable 95x reduction in the lens diameter shown in Figure 2.9. In comparison to the first experiment where the metal mesh was 70% as thick as the opening diameter, the Cr layer thickness was only 5% of the lens diameter. AFM images were not available since the AFM tip could not reach inside the lenses. Additional work by Xu [27] and Tian [28] demonstrated massively parallel etching of arbitrary nanopatterns at the bottom of each lens opening by tilting of the substrate holder relative to the beam axis. Xu's dissertation [79] also reports the deposition of 10 nm Ni nanodots with a modified source consisting of an Ar⁺ ICP with a negatively rf biased Ni target electrode placed in the plasma to generate Ni⁺ ions. The Si sample was biased at +180 V to achieve an ion landing energy of 20 eV, lower than the ~30 eV sputtering threshold energy of Ni, allowing for deposition despite a factor of 100 greater Ar⁺ ion current than Ni⁺ current.

Tian also improved the resolution of nanopantography by geometric scaling of the lenses and developing a two-step process in which patterns are initially defined in the native oxide of a Si substrate by short exposure to an Ar^+ ion beam focused by nanopantography, followed by anisotropic etching in Cl_2 plasma under highly selective photo-assisted etching conditions [28]. Using the two-step method, 3 nm holes, 7 nm wide lines, and 13 nm line-width UH logos were etched, already shown in Figure 1.3 of Chapter 1. The lens arrays used in this investigation had varying lens diameters on one sample to more efficiently find optimized focusing without repeated experiments. The 3 nm diameter were found in 230 nm diameter lenses, a 77x reduction of the lens diameter. Cross-sections of patterns formed by the two-step nanopantography process displayed nearly vertical sidewalls than patterns compared to the tapered sidewalls obtained by nanopantography alone (Figure 2.10).



Figure 2.10: (a) SEM image of feature formed by nanopantography followed by highly selective anisotropic etching versus (b) TEM image of feature formed by single-step nanopantography. Reprinted from Tian [80].

Recently, Choi et al. have reported the massively parallel deposition of 3D nanostructure arrays by focusing a charged nanoparticle aerosol jet with an electrostatic lens array, a methodology similar to deposition nanopantography [81–83]. Focusing can be done either by applying bias directly to a conducting layer deposited on top of a Si₃N₄ mask or by allowing cationic charges to accumulate on the nitride mask without a conducting layer [82]. By forming different mask patterns [81] or separating the lens array from the substrate 5 – 10 μ m and translating the substrate on a movable stage

[82,83], various 3D shapes were formed. The smallest features obtained by this method were 300 nm diameter pillars focused by cation accumulation on 4 μ m diameter circular masks, shown in Figure 2.11 [83]. While nanopantography is not referenced in these works, they are included as an example of the potential to extend nanopantography beyond etching of nanoscale features.



Figure 2.11: (a) Schematic of microlens array focusing of charged nanoparticle aerosol jets. (b) and (c) bent nanopillar structures obtained by translation of the sample stage. Adapted from Jung et al. [83]

2.4. Patterning of Graphene

Graphene is an atomically thick 2D material of great research interest due to its high electrical conductivity, unique quantum mechanical properties, and high mechanical strength. Numerous reviews of its applications in electronics, photonics, composites, energy storage, and medicine have been written [84–88]. Patterning of graphene is necessary for fabricating devices as well as modifying its properties for novel applications. Patterning approaches are typically described as either top-down or bottom-up [89]. In top-down methods, patterns are either written directly on graphene or defined on a mask and transferred to the graphene. Patterns can be precisely placed in arbitrary locations, which makes the approach particularly well-suited for making devices. However, resolution is limited by the resolution of lithography and pattern transfer, which is not yet atomically precise, and the resulting patterned edges are rough and highly damaged [89–91]. In bottom-up approaches, higher-order structures selfassemble from mixtures of molecules due to intermolecular interactions, similar to the principle behind directed self-assembly of block copolymers [89,92]. Bottom-up approaches can provide atomically precise feature sizes and atomically smooth edges [92–94], but are limited by the ability to place patterns arbitrarily, type of patterns that can be generated, and defectivity over large areas [89].

Top-down methods require pattern transfer into the graphene, typically by direct writing with energetic focused particle beams or by etching the graphene through a mask with either plasma or chemical solvents [89,95]. Ion beam irradiation of graphene is well-studied and can result in both cutting of graphene or controlled creation of defects

[96–100]. Lemme and Bell et al. were the first to report ion beam cutting of graphene with a 30 keV He⁺ focused ion beam [101,102], though pre-existing studies report cutting of carbon nanotubes with ion [103] and electron beams [104,105]. Typically, Ga⁺ ions with energy in the tens of keV are used since its relatively high mass results in a high sputtering rate of graphene [106]. However, Ga⁺ also results in large damage area, substrate damage, secondary sputtering due to collision cascades in the substrate, and ion implantation [107,108]. He⁺ ions are also widely used due to their smaller mass and collision cross section, which results in less graphene and substrate damage [97], with the potential for edge resolution up to 0.5 nm [95,107]. Low ion energy (tens to hundreds of eV) bombardment of graphene has also been studied for the controlled introduction of defects to modify electrical properties or create nanopores [96,109-112]. Molecular dynamics simulations of Ar⁺ irradiation of graphene found that isomerization of graphene is the dominant defect at ion energies below 30 eV while the creation of vacancies dominates at higher ion energies [99]. Experimental and molecular dynamics studies showed that maximum sputtering of carbon atoms in graphene by Ar⁺ occurs between 1 - 10 keV, with a yield of < 0.05 at 100 eV where displaced atoms are far more likely to be pushed towards the substrate.

Direct writing of graphene provides high resolution but is unable to provide the throughput needed for creating large patterned areas compared to pattern transfer by etching through a lithographically defined mask. Plasma etching is widely reported with oxygen plasmas [89,113,114]. Hydrogen plasmas selectively etch graphene at edges and can be used in after ion bombardment or oxygen plasma etching for lateral graphene

removal [115–117], but bulk etching of graphene does not occur without the presence of oxygen impurities in the plasma [118]. Other chemistries such as NH₃, H₂O₂, and water vapor are also of interest for functionalizing graphene [119].

Yeom et al. have reported atomic layer etching (ALE) of highly oriented pyrolytic graphite [120] and graphene with a low energy Ar neutral beam [121] and Ar⁺ ion beam [122]. In earlier investigations, shown schematically in Figure 2.12, the substrate was first exposed to a remote source of oxygen radicals generated from a plasma for 60 seconds, resulting in 19% C-O bonding, 23% sp³ bonding, and 58% sp² bonding in the graphene as measured by x-ray photoelectron spectroscopy (XPS). After oxygen exposure, plasma was turned off and the chamber was evacuated. The substrate was then exposed to 30 eV Ar neutrals generated by ion extraction from a plasma and subsequent neutralization through high aspect ratio channels formed from a stack of silicon wafers [120,121,123], which resulted in the removal of a single monolayer of graphene. However, the graphene also exhibited an increase in the number of sp³ bonds, indicating damage that was possibly due to the 48 eV peak in ion energy distribution of ions extracted from Ar plasma [120]. In later work, the sample was exposed for 90 seconds to an oxygen plasma separated from the sample by two grids that control ion energy to <20 eV followed by a 120 second exposure to <15 eV Ar⁺ ions, resulting in the removal of a monolayer of graphene [122]. Since the oxygen ion beam source can also supply oxygen radicals to the sample [124], oxygen radicals may play a role in surface oxygenation as in Yeom's previous work [120,121].



Figure 2.12: ALE of graphene from Yeom et al. [121] Top layer of graphene is modified by O₂/O radicals (a), chamber is evacuated (b), graphene is exposed to 30 eV Ar neutral beam (c), single layer of graphene is removed (d).

Chapter 3 Methods

The apparatus and general methods used in experimental studies of etching and plasma diagnostics are described in detail in this chapter. Conditions used for specific experiments will be described in later chapters in sections accompanying the corresponding results.

To TMP Gas inlet Synchronized DC bias **ICP** plasma Μ source RF power ~ 60cm Drift tube To TMP To TMP Cl₂ nozzle Loadlock Processing Motor chamber ↓ To TMP Sample Stage RFEA Top grid: Ground Middle grid: 0-120 \ Oscilloscope Α Bottom grid: -20 V

3.1. Experimental apparatus

Figure 3.1: Schematic of nanopantography experimental apparatus

Figure 3.1 shows a schematic of the nanopantography experimental system, which consists of a cylindrical ICP source, an ion beam drift tube, and a sample processing chamber. Two-stages of differential pumping were implemented to reduce the background pressure of the ion drift tube to minimize loss of ions and ion energy spread by elastic scattering and charge exchange collisions. The pressures in the 28 cm long drift tube and 21 cm long processing chamber were maintained, respectively, at 4.6 \times 10⁻⁶ and 1.5 \times 10⁻⁶ Torr at 5 mTorr with 5.4 sccm Ar flowing through the source and 2.7×10^{-5} and 2.9×10^{-6} Torr at 12 mTorr with 5.4 sccm O₂. The base pressures in the drift tube and processing chamber were 1.1×10^{-7} and 2.0×10^{-7} Torr, respectively, with no gas flow. Samples were exposed to the ion beam by placement on a two-axis rotatable sample stage in the processing chamber, 60 cm downstream from the ion beam extraction grid in the ICP source. A retarding field energy analyzer (RFEA) was installed in the process chamber (80 cm away from the plasma source) to characterize the ion beam by measuring the peak energies and half width at half maximum of the ion energy distributions.

An inductively coupled plasma (ICP) was generated in an alumina tube (12.7 cm long, 5.08 cm inside diam.), using a 3-turn water cooled copper coil (Fig. 3.2) [85] powered at 13.56 MHz by a RF power supply along with an automatic matching network (Advanced Energy, model AE Paramount Generator). A flow of Ar gas was injected into the source at a flowrate of 5.40 sccm, controlled and monitored by a mass flowrate controller (MKS-1179A21CR1BK). Teflon water tubing coiled around the alumina tube was used to cool the plasma source via closed loop chiller. A plasma

density of $\sim 10^{12}$ cm⁻³ in the ICP source was achieved at low working pressures (1-10 mTorr).



Figure 3.2: Drawing of the ICP source. [80]

3.1.1. Generation of a nearly monoenergetic Ar⁺ ion beam

Precise control of the ion beam energy is crucial for achieving sub-10 nm features through nanopantography. The minimum feature size is affected by the ion energy spread, since ions with a lower kinetic energy will be deflected at a larger angle by the lens potential than ions with a higher kinetic energy, and vice versa. The angular spread of the ion beam source must also be minimized by keeping the beam space charge neutralized to avoid Coulombic repulsion of beam ions. And finally, the lens potential

required to achieve the minimum feature size is a function of both the mean ion energy and spread of the ion energy distribution as will be discussed in Chapter 5.

A technique developed by Xu et al. [71], adapted for a cylindrical ICP, was used to extract a nearly monoenergetic ion beam from a power modulated (pulsed) plasma through a grounded metal grid by applying a synchronous DC bias on a boundary electrode in contact with the plasma (see Fig. 3.1). The DC bias was generated by synchronizing the pulse-power modulated signal and amplified by a high voltage pulse generator (AVTECH AVR-3-PS-PP-UHF). A single grounded grid (W mesh with 200 µm square openings and 84% transparency) covered a 5 mm diameter aperture in the cylindrical plasma source on the side opposite of the boundary electrode. When no voltage is applied to the boundary electrode, the plasma potential, V_p , is expected to be ~4.8Te above ground potential. Langmuir probe measurements [77,80] during the power-on and late afterglow (power-off) fractions of the cycle yielded respective values of 4.5 and 0.2 eV for T_e , and 26 and 0.3 V for V_p , reasonably close to the expected values. In the afterglow of the pulsed plasma, a synchronized DC bias voltage, V_{bias} was applied on a boundary electrode in contact with the plasma, raising the plasma potential close to $V_{bias} + V_p$. This caused positive ions to be expelled from the plasma through the ion extraction grid. As time continues into the afterglow, the plasma potential drops to near zero and the ions form a nearly monoenergetic ion beam with ion energy controlled by the applied DC bias, as shown in green arrows in Figure 3.1.

An example of the pulsed-power and synchronous boundary bias voltage timing is shown schematically in Figure 3.3, with conditions used from etching of Si samples with an Ar⁺ ion beam. The RF power (800 W peak at 13.56 MHz) to the ICP was modulated at 10 kHz (100 μ s period). The active glow (power-on) commenced at t = 0; power was turned off (beginning of the afterglow) at $t = 20 \ \mu$ s, (i.e., a duty cycle of 20%). A 100 V DC bias (V_{bias}) voltage was applied to the boundary electrode 20 μ s into the afterglow ($t = 40 \ \mu$ s), lasting 20 μ s. A new cycle started at $t = T = 100 \ \mu$ s. For an argon ion beam, the gas pressure in the ICP source was kept at 5.0 mTorr and Ar gas flow rate was 5.4 sccm. For etching of carbon containing samples with an oxygen ion beam, the duty cycle and gas pressure in the ICP were increased to 65% and to 12.0 mTorr, respectively, while the delay between plasma-off and bias-on (Δt_{delay}) and the bias duration (Δt_{bias}) were decreased to 15 μ s.



Figure 3.3: Schematic of the pulsed plasma power and bias sequences for Si etching experiments with an Ar⁺ ion beam.

It was shown by Chen et al. that the extracted positive ions formed a nearly monoenergetic ion beam with self-neutralized space charge by periodic injection of electrons into the downstream region of the extraction grid, primarily during the early afterglow. No hot filaments or other external sources of electrons were employed to neutralize the space charge of the beam. A background plasma (electron density $\sim 10^{10}$ cm⁻³) is formed by these electrons, in conjunction with relatively low-energy ions (1– 10 eV) that emerge out of the ICP when the DC bias is off, as well as formed by resonant charge exchange of the 70-100 eV beam ions with the background Ar in the downstream region nearest to the extraction grid.

3.2. Measurement of Ion Energy Distribution Using a Retarding Field Energy Analyzer

Precise measurement of the ion beam energy is crucial for achieving the smallest possible features through nanopantography. The optimum lens potential to focus the ion beam is a function of both the mean ion energy and the ion energy spread, which are subject to day-to-day variation and should be measured before each etching experiment. A retarding field energy analyzer (RFEA), installed 80 cm downstream of the extraction grid of the ICP source (figure 3.2) [85], as shown in Figure 3.4, was used to measure ion energy distributions (IEDs). A 2.5 cm diameter hole concentric with the ion beam axis was bored into the rotatable sample stage to allow measurement of the ion energy distribution without removing the stage so that IEDs could be measured before each etching experiment.



Figure 3.4: Schematic of system setup for ion energy distribution measurement. The sample stage is not shown but was present in the sample processing between the RFEA and source.

The RFEA was made of a stack of three parallel Ni grids, each with 40 μ m square openings and 85% transparency, spaced 1.5 mm apart from one another, and a stainless steel, grounded current collector, spaced 5 mm from the bottom grid (Fig. 5.1). The top grid was grounded. A 1 Hz, 0 to 120 V sawtooth waveform was applied to the middle

(energy selector or discriminator) grid (held on a 5mm diam. aperture), using a Stanford Research Systems DS345 function generator amplified with an AVTECH AV-112H-PS-UHA high voltage amplifier. The bottom grid was biased with a DC voltage of -20 V to suppress secondary electron emission from ions striking the current collector plate. The total transparency of the three-grid stack was approximately 60%. A Keithley 6485 pico-ammeter was used to measure the collector current as a function of voltage applied to the middle grid. Data were recorded by a four-channel oscilloscope (Agilent Technologies DSO-X 2024A) and smoothed by averaging 1024 current–voltage (*I–V*) curves to reduce noise.

An example of a measured I-V curve and associated IED is shown in Figure 3.5 for an Ar^+ ion beam generated by the previously detailed methods with 70 V synchronous DC bias. The total ion current from the collector is the sum of low energy (<40 eV) ions exiting the source before bias is applied to the boundary electrode and the high energy ions corresponding to the boundary bias potential, with each element comprising about half the total time-averaged ion current measured by the picoammeter. The ion energy distribution is found by taking the derivative of the I-V curve with respect to voltage (equivalent to ion energy in eV). For each set of operating conditions examined, a Gaussian curve was fitted to the peak ion energy with baseline set to zero. Only the high energy ion beam current, found by integrating the area under the Gaussian fit, is available for etching since the bias applied to the conducting electrode of the lens arrays rejects ions with energy lower than the focusing voltage.



Figure 3.5: I-V curve (black) and IED (blue) of Ar+ ion beam generated under 5 mTorr, 800 W peak power, 10 kHz pulsing at 20% duty cycle, 70 V synchronous DC bias applied 20 µs into the afterglow. Gaussian peak fit shown in red.

Chapter 4 Print and Repeat Nanopantography with Removable, Reusable Electrostatic Lens Arrays

Previous work in nanopantography has demonstrated etching of silicon and deposition on the sub-10 nm scale with Si/SiO₂ lens arrays fabricated directly on the silicon substrate [26,28,79,80]. While it may be possible to fabricate lens arrays on other substrates, lenses would still need to be fabricated and removed multiple times in a manufacturing process requiring multiple patterning steps, increasing the time for process development and the chance of defects. A promising low-cost proposal that addresses both problems is to use lens arrays that can be clamped onto a substrate, activated for patterning, removed, and repositioned on the same substrate or reused on a different substrate in a method called print-and-repeat nanopantography. This method has the potential to make nanopantography useful for manufacturing devices for research and small-scale applications where EUV lithography would be cost prohibitive.

This chapter details the process of developing removable and reusable membrane-based electrostatic lens arrays for print-and-repeat nanopantography, including key considerations and fabrication steps. Patterning of silicon substrates with an argon ion beam in a background of chlorine gas was also demonstrated. The effect of lens diameter on feature size on the focal plane was investigated via experiments and SIMION ion optics simulations.

4.1. Removable Lens Development

4.1.1. Material Considerations

To achieve sub-10 nm nanopantography with removable lens arrays, lens materials must be selected carefully. The lens arrays must be flexible enough to resist fracture during handling, electrostatic clamping to the substrate, and release from the substrate. Additionally, the lens dielectric material must have a sufficient dielectric strength that the fabricated lens arrays can focus up to 100 eV Ar⁺ ions, which are necessary to etch Si with an etching yield of 0.7 [125,126]. In the present study, lens arrays had a dielectric thickness of 1 μ m, necessitating a dielectric strength of at least 100 V/ μ m.

Previously, removable lens arrays were fabricated using silicon nitride as the dielectric material, which were brittle and easily fractured during handling [127]. SU-8 was ultimately selected as the material for the lens dielectric since it can easily be spun onto a substrate with controlled thickness, has a dielectric strength of around 120 to 400 V/ μ m [128], and is more flexible and robust than silicon nitride. In this study, the SU-8 layer was 1 μ m thick, which allowed the lens array to reliably sustain an applied voltage of 100 V, approximately the voltage necessary to focus 100 eV Ar⁺ ions.

4.1.2. Fabrication Overview

An overview of the lens array fabrication process is shown in Figure 4.1. The lens arrays were fabricated on a silicon wafer spin coated with a polymethyl glutarimide (PMGI) sacrificial layer and 1 µm SU-8 (Microchem SU-8 2005, 3000 rpm) dielectric

layer. Next, 30 nm of gold followed by 30 nm of copper are thermally evaporated onto the SU-8 through a mask placed over the wafer with 1 x 1 cm openings for each lens array, forming the conducting layer of the lens. For the final deposition step, 100 nm of PMMA resist was spin coated onto the copper to form a resist layer that can be patterned via atom beam or electron beam lithography. The thickness of the PMMA is limited by the lithography method, and for the helium atom beam lithography used in the present study the maximum thickness was 100 nm. Lens openings were lithographically defined on the PMMA, and an acrylic frame was bonded to the array with a thin layer of doublesided adhesive to allow handling of the lens array after release from the wafer.



Figure 4.1: Schematic of removable lens fabrication process with a photograph of the bottom side of the membrane (facing the substrate). Courtesy of Basu [129].

The lithographically defined lens patterns were transferred through the copper by sputtering with an Ar^+ ion beam using PMMA as the mask, which has a selectivity of 1:1. After the copper was broken through, the pattern was transferred through the SU-8 using copper as the mask via etching in an O_2 plasma with an overetch into the PMGI. Since the selectivity between SU-8 and gold was only 17:1 under the oxygen etching conditions, the gold must be protected by the copper layer, which had a selectivity of 70:1 between SU-8 and copper after chamber conditioning with SF_6 plasma. Finally, the membrane was released from the wafer by dissolution of the PMGI layer in tetramethylammonium hydroxide (TMAH) solution (Dow Microposit MF-319 Developer) for a minimum of 2 to 3 hours at 40°C. After separation from the wafer, the lens arrays were placed in a fresh bath of TMAH for 15 minutes to eliminate leftover PMGI residue that may have redeposited on the sidewalls and then were thoroughly rinsed with deionized water and allowed to dry in air for at least 12 hours. After drying, a thin layer of silver paste (PELCO® Conductive Liquid Silver Paint #16034) was painted along the top and sidewalls of the frame with a fine paintbrush to provide a electrical contact to the sample stage and a conducting path to the Cu/Au lens electrode on the membrane. Caution must be exercised to avoid allowing too much silver paste onto the membrane as it may seep into gaps between the membrane and frame that may have formed during soaking in TMAH, causing an electrical short-circuit between the lens electrode and substrate. Typical resistance measurements between silver painted

contacts on opposite sides of the frame were ~15 Ω , indicating excellent electrical connections.

4.1.3. Lens Clamping

While the lens arrays appear to be flat during fabrication, most lens arrays appear to have wrinkles after releasing due to factors such as uneven tension from the placement of adhesive or thermal expansion and contraction from heating during Ar^+ sputtering and RIE. Furthermore, lens arrays may become wrinkled after placement onto and removal from a substrate as shown in Figure 4.2 (left).



Figure 4.2: Photograph of lens array previously used in nanopantography before (left) and after clamping on a silicon substrate by +100 V applied bias (right). The same lens array is shown in both photographs.

Fortuitously, the applied potential used to focus the ion beamlets during nanopantography simultaneously serves to electrostatically clamp the membrane to the substrate surface under the same principle that enables electrostatic chucks to be used in commercial plasma processing tools. When a bias is applied to an electrode separated from a conducting substrate by a dielectric layer, an attractive force arises from the temporary migration of an opposite surface charge on the conducting substrate. The electrostatic clamping pressure in vacuum between the metal electrode layer of the lens array and the substrate is given by

$$P(Pa) = \frac{\varepsilon_0}{2} \left[\frac{\kappa V}{d + \kappa g} \right]^2 \tag{4.1}$$

where the permittivity of free space, $\varepsilon_0 = 8.85 \text{ x } 10^{-12} \text{ F/m}$, κ is the dielectric constant of the insulating layer, V = the voltage on the metal layer of the lens array, d = dielectric layer thickness, and g = gap size between the top of the substrate and the adjacent surface of the dielectric layer. This relationship is also plotted below in Figure 4.3. In the present investigation, $\kappa = 4.1$ for SU-8 [130], V = +100 V, and $d = 1 \mu \text{m}$. If g can be assumed to be on the order of the membrane thickness d, a pressure of 0.28 atm is exerted on the free-standing portion of the membrane. As the membrane is pulled closer to the substrate surface, the electrostatic clamping pressure increases to 1 atm at g = 0.4 μm and a maximum of 7.3 atm when the SU-8 is in perfect contact with the substrate surface. While portions of a wrinkled membrane are raised in excess of 1 μm , the electrostatic pressure exerted on a region near the edge of a wrinkle is significant enough to flatten the membrane against the substrate surface and smooth out existing wrinkles, allowing for intimate contact between the membrane and substrate as shown in Figure

4.2, right. As long as a portion of the membrane is in contact with the surface, flattening of the membrane onto the surface should be able to propagate throughout the entire sample.



Figure 4.3: Clamping pressure vs gap size, g, as given in Equation (4.1).

To give additional confirmation that the lens array is in contact with the substrate, clamping is also verified in-situ by determining the capacitance of the lens array before and after application of +100 V to the lens electrode. A diagram of the circuit used to determine lens array capacitance is shown below in Figure 4.4. The lens

array is placed on a highly doped, p-type silicon substrate (.001-.005 Ω -cm) mounted on the sample holder, then placed in vacuum in the processing chamber. A 200 kHz, 2 V peak-to-peak voltage is applied to the lens array by electrical connection to the bottom of the silicon substrate. The top of lens electrode is connected to the positive terminal of the DC power supply normally used to apply bias to focus the lens array, operated at 0 V and +100 V. The negative terminal of the DC power supply is connected to ground via a 200 Ω resistor. The peak-to-peak voltage across the 200 Ω resistor is measured through an oscilloscope and the capacitance of the lens array is determined from a capacitance calibration curve (Figure 4.5) constructed from the exact same circuit with capacitors of known values in place of the lens array.



Figure 4.4: Diagram of capacitance measurement circuit. For calibration, the portion marked "Lens Array Equivalent Circuit" is replaced by known capacitors. The same equipment and wiring are used for both procedures.



Figure 4.5: Calibration curves constructed from circuit shown in Figure 4.4 with capacitors of known capacitance replacing the lens array. Measurements were conducted at 3 frequencies.

The fraction of the membrane in contact with the surface is estimated by comparing the measured capacitance of the lens array to a parallel plate capacitor model consisting of a fraction of the membrane directly in contact with the substrate, $x_{contact}$, in parallel with the remaining fraction of the membrane separated by an air gap g. The capacitance is given by

$$C = \frac{\kappa \varepsilon_0 A}{d} x_{contact} + \frac{\kappa \varepsilon_0 A}{d + \kappa g} (1 - x_{contact})$$
(4.2)

where κ is the dielectric constant of the insulating layer ($\kappa \sim 4$ for SU-8 at 200 kHz [130]), A = the area of the lens array covered by the metal lens electrode (0.49 cm²), d = dielectric layer thickness (1 µm), and g = gap size between the top of the substrate and the adjacent bottom surface of the dielectric layer of the lens array.

In the case of perfect contact between the dielectric and the substrate, g is zero and the maximum capacitance is 1.78 nF. In the case that g is initially small ($<1 \mu m$), the clamping pressure of 0.28 to 7.3 atm is expected to flatten the membrane against the surface upon application of +100 V bias. On the other hand, if g is initially large (> 1 μ m), typically caused by dust particles, the capacitance resulting from the gap is much smaller than 1.78 nF which allows the second term of Equation (4.2) to be neglected and the fraction of the membrane in contact with the substrate can be estimated as the measured capacitance divided by the maximum expected capacitance of 1.78 nF. Curves showing the relative contribution of the membrane and assumed gap to the total capacitance for each case are shown below in Figure 4.6. Total capacitance including gap is shown in black while the capacitance due to portions of the membrane in intimate contact with the substrate are shown in red. Blue dashed lines indicate contact fractions for significant measured voltage V_M and corresponding lens array capacitances C in this study. Lens arrays typically showed less than 30% contact ($V_M < 20$ mV measured at 200 kHz) when first placed on a substrate, without any bias applied. After application of +100 V bias, typical V_M ranged between 40 mV and 50 mV at 200 kHz, indicating a total capacitance of 1.1 to 1.38 nF. If it is assumed that any dust particles are typically

larger than 10 μ m, then the typical capacitance values after clamping indicate 60-80% contact.



Figure 4.6: Equation relating capacitance to fraction of the membrane in contact with the substrate surface for varying assumed gap sizes, *g*.

4.1.4. Clamped Lens Release

After electrostatic clamping, significant attractive forces exist between the trapped surface charges on the SU-8 dielectric and the substrate surface, which can remain indefinitely unless there is a mechanism to release the trapped charges. In electrostatic chucks, multiple methods have been used such as application of a variable

low-frequency (<50 Hz), high voltage [131] or exposure of the sample to a plasma after removing the clamping voltage [132,133]. It has also been found that the electrostatic clamping force in electrostatic chucks is sensitive to humidity. At atmospheric pressure and 50-60% relative humidity, the clamping force was found to be lowered to 1/3 of the force in vacuum at the same clamping voltage whereas the clamping force was equal to the vacuum clamping force in a background of dry nitrogen gas at atmospheric pressure [134]. It was proposed that the diffusion and dissociation of water molecules in the high electric fields at the interface between the silicon substrate and chuck facilitates charge transport, freeing trapped charges [135,136]. For the present investigation, ultrapure deionized water was used to declamp the lens array from the substrate surface. After clamping to the silicon surface via application of bias during an etching experiment, the sample was removed from vacuum and water was dropped on the outer edge of the acrylic frame, between the silicon substrate surface and frame. The water diffused under the membrane, lifting the membrane off the silicon and suspending the membrane on the surface of the water where it could be easily removed. This allowed lens arrays to be reused in nanopantography experiments even after clamping, as demonstrated in section 4.2 below.

4.2. Experimental Etching Results

4.2.1. Proof of Concept Experiment

Previous results from Xu and Tian have demonstrated that nanopantography can pattern features up to 100x smaller than the size of the lens opening [26–29]. However, these features were etched with lenses fabricated directly on silicon substrates and no previous work has demonstrated nanopantography with removable lens arrays.

Proof of concept experiments were conducted using lens arrays with 1.4 µm diameter lens opening and 1 µm SU-8 dielectric layer placed on a highly doped p-type Si substrate. The bottom of the silicon substrate was scratched with a diamond scribe and painted with silver paste (PELCO® Conductive Liquid Silver Paint #16034) to form an electrical connection to system ground via the sample stage. The sample was then loaded into the processing chamber and positioned perpendicular to the ion beam direction. +70 V of bias was applied to the metal layer to clamp the lens array to the substrate and the percent contact was measured to be approximately 70%. A nearly monoenergetic Ar^+ ion beam was generated using the methods described in Chapter 3, using a +70 V bias on the boundary electrode to generate a mean ion of 70.2 eV. The metal layer on top was biased with a +63.2 V dc voltage. Chlorine was admitted into the processing chamber with partial pressure of 3.0 to 4.0×10^{-5} Torr. The nearly monoenergetic Ar+ ion beam had a measured peak energy of 70.2 eV with a full width at half maximum (FWHM) of 5 eV. The ion beam current density at the sample location was measured to be $0.3 \,\mu$ A/cm². The sample was exposed to the ion beam for 6 minutes. After etching, the frame of the lens array was removed by cutting around the edge of the membrane with a scalpel. The membrane was also sliced through the patterned area to reveal the cross sections of individual lenses and to aid in focusing on etched features

on the substrate surface. The sample was examined under scanning electron microscopy as shown in Figure 4.7.



Figure 4.7: SEM images of 100 nm holes created by nanopantography with 1.4 μmdiameter removable lenses. Top: top-down view of the silicon with lens array in the foreground. Bottom: 45° tilted view of lens and silicon interface.

From the top down view, the lens openings appeared to be mostly round, with edge roughness on the metal lens openings on the order of 20 to 30 nm. This roughness is transferred from the atom beam lithography masks, which display striated sidewalls after oxygen plasma etching of the SU-8. The SU-8 sidewalls on the lens arrays are also not perfectly smooth and have noticeable striations on the order of 40 to 70 nm that do not exactly follow the roughness in the metal mask. Striations in SU-8 were found to be due to contamination and redeposition of antimony used in the photoacid generator of the SU-8 and can be minimized by addition of fluorine in the form of SF_6 to O_2 plasma [137]. The SU-8 was undercut approximately 80 nm behind the edge of the metal lens opening, indicating a 7% undercut due to isotropic etching. Examination of the interface between the lens and the substrate surface shows that there was no visible gap between the bottom of the membrane and the substrate surface, confirming that the SU-8 was in intimate contact with the silicon surface after electrostatic clamping via application of bias. In fact, the membrane remained in contact with the silicon surface even after cutting with a scalpel, indicating that trapped electrostatic charges continue to exert a clamping pressure, securing the membrane to the silicon even after removal of bias. The center of the etched feature on the silicon surface was offset from the center of the lens opening on one axis by 120 nm, indicating that the sample was tilted 6 to 7° with respect to the ion beam axis assuming an SU-8 thickness of 1.1 to 1 µm. In fact, measurements of the SU-8 thickness from the 45° tilted side view of the cut membrane indicate that the true SU-8 thickness is approximately $1.1 \,\mu\text{m}$. 100 nm diameter holes were etched onto the silicon surface at the bottom of each lens opening, which is much larger than the

expected size of 14 nm based on a 100x reduction of the 1.4 µm lens diameter from previous work. This indicated that the bias applied to the metal electrode on the lens was not the optimal voltage to focus the incoming ions to a focal point on the plane of the substrate surface and the ions may either come at a focus above the plane of the substrate (over-focused) or under the plane of the substrate (under-focused). However, it is not possible to distinguish between over-focusing and under-focusing due to the cylindrically symmetric lens openings versus the rounded square lens arrays used in previous work. While the minimum feature sizes were larger than previous results with lenses fabricated directly on the silicon surface, the preliminary etching results still demonstrated that etching with removable and reusable membrane-based lens arrays is possible.

4.2.2. Effect of Lens Geometry

While nanopantography is capable of 100x reduction of the lens diameter, this requires optimization of ion beam characteristics, lens focusing voltage, lens aspect ratio, and etching time. Simulations can aid with optimization as shown in Chapter 5, but due to slight variations in peak ion energy, ion energy spread, and lens dimensions, trial and error is necessary to achieve the smallest possible feature sizes. Since only one set of experimental conditions can be investigated in a single etching experiment conducted, lens arrays were fabricated with lens diameters between 800 nm to 1.5 μ m in 100 nm increments and nominal SU-8 dielectric thickness of 1 μ m to study the effect of lens aspect ratio on feature size and to aid in generating the smallest possible feature

size for a given run. Lens arrays were placed on highly doped p-type silicon substrates and capacitance was measured before and after application of +70 V bias to electrostatically clamp the lens array to the silicon. Biases between +63 V and +72 V were applied to focus the Ar^+ ion beam, which typically had a peak ion energy of 70 eV with 4 eV FWHM and ion flux of 0.2 μ A/cm² at the sample. After etching, the samples were inspected in SEM with the lens array still attached to the substrate, a step that was found to be necessary due to the low contrast of etched feature on pure silicon. After locating the patterned regions and imaging the etched features through the lens openings, the SEM chamber was vented to atmosphere and water was dropped between the outer edge of the lens array and silicon surface, which allowed the lens array to be removed non-destructively and reused. The silicon surface was dried with dry nitrogen, and the sample was returned to vacuum in the SEM, without removal or repositioning of the substrate or substrate holder, allowing etched features to be easily located since the beam was already in a patterned area with optimized focus and contrast settings. Each substrate was used to etch only one hole with a single combination of etching time and focusing voltage while lens arrays were reused between substrates until they were rendered unusable due to electrical breakdown or damage during handling.


Fig. 4.8: SEM images of holes etched by print-and-repeat nanopantography with 800 to 1.5 μ m diameter lenses exposed to a 72.3 eV Ar⁺ ion beam at +71.2 V bias for 30 minutes.

Feature size measurements versus lens diameters are shown in Table 4.1. Fig. 4.8 shows SEM images for an experiment where the substrate was exposed to a 72.3 eV ion beam with +71.2 V bias (98.5% of the peak ion energy) for 30 minutes. At 800 nm lens diameter, the feature size was approximately 110 nm, which is only a 7.3x reduction in the lens diameter. At 900 nm lens diameter, the feature size decreased to 90 nm (10x reduction), indicating that the focal plane is moving towards the substrate and the focusing voltage was too high for these narrow aspect ratios, a result of over-focusing where the ion focal plane lies above the substrate surface. As the lens diameter increases at a fixed dielectric thickness, the focal plane of the image moves farther away from the lens opening due to a decrease in the electric field strength inside the volume of the lens. At 1 µm lens diameter, the image rapidly moved into focus and the spot size decreased sharply to 24 nm, which is a 42x reduction of the size of the lens opening and the smallest feature size obtained by print-and-repeat nanopantography so far. At 1.5 μ m, the smallest feature size is 30 nm which represents a 50x reduction of the lens diameter, the largest reduction in size of the lens opening for print-and-repeat nanopantography and only a factor of 2 larger than the 100x reduction obtained from nanopantography with lenses fabricated directly on the substrate. From 1 μ m to 1.5 μ m lens diameters, the feature size remained between 20 to 30 nm, as shown in Table 4.1. This result was somewhat unexpected, since the focus and feature size was expected to be sensitive to a specific combination of lens aspect ratio, ion energy, and focusing voltage. Further investigation of this effect is discussed below and in simulations conducted in Chapter 5.

Lens Diameter	Smallest Feature	Lens Diameter
(nm)	Size (nm)	Reduction
800	110	7
900	90	10
1000	24	42
1100	34	32
1200	26	46
1300	30	43
1400	37	38
1500	30	50

Table 4.1: Smallest feature sizes and lens diameter reduction measured by SEM for varying lens diameters. Etching conditions were 72.3 eV ions, 0.2 μ A/cm² ion current, +71.2 V focusing voltage, 30 minutes exposure to beam.

SIMION ion trajectory simulations were also conducted using the same lens geometries and ion beam conditions in order to compare expected feature sizes to those measured in the previous experiment. Details of simulation assumptions, geometry, theory, and limitations will be discussed in Chapter 5. The simulations provide a distribution of ion positions on the plane of the substrate surface, and the FWHM of the distribution of radial positions from the center of the lens was taken as the expected feature size. The simulations predicted a minimum expected feature size of 32 nm, which occurs between 800 nm to 1.1 μ m lens diameter. While the image is over-focused only for lens diameters smaller than 800 nm in the simulation (shown in the red shaded region on the left of Fig. 4.9), experiments showed an over-focused image for lens diameters smaller than 1 μ m (shown in the gray shaded region on the left of Fig. 4.9). Simulations also showed the beam moves out of focus at lens diameters larger than 1.1 μ m while the beam remained in focus even up to 1.5 μ m. It is likely that the SU-8 layer may be thicker than 1 μ m, as seen with lens arrays used in proof of concept experiments, causing the focal plane to move upward relative to the sample surface for a given lens diameter. This leads to a widening and shift to the right of the optimum focal range for the simulated focus curve in Fig. 4.9. Both the experiment and simulations show that lens diameter can vary around 15% while keeping the image in focus.



Fig. 4.9: Comparison of experimental and SIMION simulated etched feature sizes with varying lens diameters for a 1 µm thick SU-8 dielectric lens array.

It is important to realize that the simulation does not include the effects of etching yield, etch rates on different materials, or exposure time, so caution must be taken when comparing simulations to etching results. For example, the native oxide has a different etching rate than the underlying silicon and careful optimization of the ion energy and exposure time can result in feature sizes much smaller than predicted in simulation. Naturally, a shorter exposure time (less ion fluence) will result in a smaller feature if etching is only allowed to proceed for a few ions to break through the surface at the center. This strategy was used by Tian in combination with highly selective chlorine plasma etching to pattern 3 nm holes at the bottom of 300 nm diameter lenses [28].



Figure 4.10: Ion radial distribution (red) and Gaussian fit (blue) at the plane of the silicon surface for lens diameters 800 nm to 1.4 μ m. Simulated ion beam and focusing conditions match experimental conditions.

Additionally, the shape of the ion spatial distribution at the sample can deviate quite significantly from a Gaussian distribution and lens shapes with the same FWHM can have different base widths and peak heights. Fig. 4.9 shows that the 800 nm diameter lens and 1.1 µm diameter lens are expected to have the same feature size based on the FWHM, yet the radial distributions shown in Figure 4.10 for 800 nm lens diameter has a much wider base (400 nm vs 100 nm for 1.1 µm lens diameter). This also contributes to the experimental observation that the feature size with 800 nm diameter lens was larger than the feature size with 1.1 µm diameter lens (110 nm vs 34 nm, respectively). These considerations are analogous to optical lithography, where beam intensity at the focal plane, exposure, and resist sensitivity must be balanced to maximize contrast when exposing photoresist. Nevertheless, there is reasonable agreement between the simulation and experimental results demonstrating that this method of ion trajectory simulation can be used to predict etched feature size. Simulations can also provide valuable information about the shape of the radial distribution of ions at the substrate plane, guiding the choice of appropriate experimental conditions.



Figure 4.11: AFM false-colored images of 800 nm, 1 µm, and 1.5 µm diameter lenses on left, with line scans corresponding to markings shown on right.

In the SEM images of the silicon surfaces (Fig. 4.8), several variations in the false coloring can be seen on different areas of the silicon surface, including the area covered by the SU-8 membrane and unexposed to the beam, the outline of the lens on the silicon exposed to the beam, sharp dark spots where the etched features are located, color differences around the circumference of the etch spots, and bright white spots usually located near the etch spot. These colors arise from changes in detector intensity of electrons due to height, angle, and material reflectivity differences. However, SEM does not provide any information on the relative height of regions or identity of materials, so these effects are convoluted together. Atomic force microscopy (AFM) scans of the silicon substrate surface were performed to gain more insight on the etch profile and features, selected scans for 800 nm, 1 μ m, and 1.5 μ m lenses are shown in Figure 4.11.

The scans show that the area inside each lens opening is raised 6 to 8 Å relative to the adjacent silicon surface covered by the SU-8. Since the bias applied to lens electrode causes ions with sufficient energy to be focused to the center of the lens opening and ions with energies lower than the focusing voltage to be rejected, the modification of the silicon surface inside the lens opening must come from uncharged particles that are unaffected by electric fields. Possible sources include contamination from sputtering of materials in the plasma source, VUV photon emission from the plasma, and high energy neutrals generated from resonant charge exchange collisions between Ar^+ ions at the peak ion energy with a background of Ar gas in the downstream region near the extraction grid. VUV photon emission can be ruled out, since the outlines of the lenses on the silicon display feature definition much smaller than 50 nm, well below the wavelength of VUV photons. Neutral bombardment is a possibility since resonant charge exchange was found to be a major loss pathway for high energy Ar^+ ions near the exit of the extraction grid, which had a pressure of 0.12 mTorr 5 cm downstream of the extraction grid at 5 mTorr ICP pressure [77]. The neutrals generated must be energetic enough to create silicon dangling bonds on the surface, which react with oxygen and water vapor to form SiO_2 upon removal of the sample from vacuum, and/or from the residual background gas in the chamber (likely water vapor) during processing. However, if neutral bombardment is the cause then the neutral atoms must also have a low enough energy to avoid etching.

Another unidentified feature present in the SEM scans were one or two bright spots less than 10 nm in diameter on the surface of the silicon, typically within 50 nm of the etched feature. AFM height measurements revealed that these features were on the order of 10 to 20 nm taller than the surrounding silicon. Due to their size and height, these features are not likely to be dust particles or contamination introduced by the water declamping process since dust is typically on the order of tens to hundreds of microns and the features were present even before water was dropped on the sample. Furthermore, these features were not present in the unoptimized proof of concept experiments in which 100 nm holes were etched, though they may have been etched away due to the larger diameter of the out of focus beamlet. The bright features are also absent in SEM scans of the 800 nm diameter lenses, supporting this hypothesis. Ultimately, the source and identity of these features cannot be revealed without the use of analytical techniques that can provide space-resolved composition information on the sub-micron scale.

Etched feature size measurements using SEM were found to vary significantly from AFM measurements. Measuring feature diameters in SEM tends to be subjective due to the lack of depth information, beam drift, and differences in focus and contrast between measurements. Feature edges imaged via SEM can only be identified when the depth of the feature changes enough to cause a significant contrast change relative to the surrounding surface while AFM detects height changes larger than noise (approximately 2 Å). As shown on the right column of Figure 4.11, AFM measurements of the width of the opening at the top of etched features were more than 100 nm for all lens sizes. 1.5 µm diameter lenses were found to have etched features with diameter 250 nm, even though SEM measurements were around 30 nm. AFM size measurements taken halfway to the bottom of the feature (i.e. FWHM) showed a closer match to SEM measurements taken from the top down.

4.3. Summary

A process was developed for fabricating reusable membrane-based electrostatic lens arrays for the nanopantography patterning method. Lens arrays were fabricated on silicon wafers using 1 μ m of SU-8 as a dielectric material and copper and gold as the lens electrode. The lens arrays were placed on silicon substrates and biased to +100 V to demonstrate flattening and electrostatic clamping to the substrate surface. The lens arrays were used to etch features on silicon and examined under scanning electron microscopy and atomic force microscopy. Experiments were conducted to compare the effect of lens geometry on feature size at a fixed lens focusing voltage and the results were compared to SIMION ion optics simulations. The removable lens arrays were successfully used to pattern 30 nm features using a 1.5 μ m diameter lens array, a size reduction of 50X. These results demonstrate the feasibility of using reusable and removable membrane-based electrostatic lens arrays for nanopantography.

Chapter 5 SIMION Simulations of Nanopantography Lens Focusing

While print-and-repeat nanopantography was successfully demonstrated in Chapter 4, the smallest features achieved so far were 30 nm, versus 3 nm features using 300 nm diameter lenses fabricated directly on the substrate. Processing tricks can be used to maximize selectivity between the silicon and native oxide, but ultimately the ability to precisely focus ion beamlets entering each electrostatic lens into the smallest possible spot on the substrate surface governs the resolution of nanopantography. The minimum spot size is not arbitrarily small and is limited by lens geometry and aberrations analogous to conventional optics. While extensive experimental studies can be done, the size of the parameter space to investigate combined with the effort needed to fabricate and inspect samples can consume time while yielding limited information on the underlying physical phenomena. Furthermore, ion focusing requires the selection of an focusing voltage based on the ion energy distribution, which is a system property that may vary from day to day. Ion trajectory simulations are a quick, computationally inexpensive modeling approach that can help understand the effects of various aberrations and find the optimum focusing voltage before experiments are conducted. SIMION is an ion optics simulator widely used in the design of focused ion beam systems and mass spectrometers and can model ion trajectories in 2D axisymmetric and full 3D electrostatic and magnetic fields [138]. In this chapter, SIMION was used to

study the effects of lens geometry and ion beam properties to guide the choice of optimum processing conditions and understand limitations on feature size.

5.1. Methods

The nanopantography system contains phenomena occurring over distances that span several orders of magnitude, ranging from the transport of the beam through the drift tube over the meter scale, Coulombic interactions between ions on the centimeter scale, ion focusing in sub-micrometer scale lenses, to etching on the nanoscale. Since direct simulation over these disparate length scales is computationally prohibitive, the model of the system was divided into two domains: the macroscopic ~60 cm ion drift region starting from the exit of the ion beam source up to the microscopic ion focusing region starting 3 µm away from the lens openings. Modeling in both domains assumed no collisions or Coulombic interactions between ions. Radial positions were randomly generated over the diameter of the of the source and experimentally measured ion beam properties were used as initial conditions to solve for ion velocity vectors and positions at the end of the analytical domain using conservation of energy. The final particle positions and velocity vectors at the end of the analytical domain.



Figure 5.1: Schematic of modeling regions. Macroscopic analytical domain is shown with white background. SIMION domain is shown with gray background, overlapping with sample stage region. Schematic is not drawn to scale.

5.1.1. Macroscopic Domain: Analytical Solution

A schematic of the system model is shown in Figure 5.1. The macroscopic domain is further divided into two regions: the field-free ion "drift region" that extends from the exit of the source to the aperture of the top grounded plate of the sample stage and the "sample stage region" that begins on the other side of the aperture and extends to the lens electrode surface where the SIMION simulation domain begins. The aperture of the grounded cover plate is covered by a nickel mesh, creating a region of zero electric field between the exit of the ion beam source and the grounded cover plate. The other side of the grounded cover plate facing the substrate has an electric field in the 1 cm distance between itself and the sample cover plate, which is biased at the focusing potential (typically +70 to +100 V) and electrically connected to the metal electrode of $\frac{70}{70}$

the lens array. The sample cover plate is the exact same size and shape as the grounded cover plate, differing only by the lack of nickel mesh. Since the 1.6 cm gap between the grounded plate and the sample is small compared to the dimensions of the sample cover plate, the electric field is approximately uniform in this region.

An ion exiting the source a distance from the axis of symmetry r_s has an initial axial velocity v_x and a radial velocity v_y , giving it an angle of $\theta_1 = \tan(v_y/v_y)$. Since there are no electric fields in this region, the ion will travel through this region a distance of $d_{SM} = 60$ cm, reaching the aperture of the grounded cover plate with unchanged velocity vector and angle. Once the ion passes through the aperture, it will experience deceleration in the axial direction due to the voltage applied on the sample cover plate and lens electrode, V_L , which decelerates incoming positive ions from the beam over a distance of $d_{ML} = 1.6$ cm and causes an increase of the angle of incidence of the ion to a certain angle θ_2 as it enters the SIMION simulation domain. To calculate θ_2 , an energy balance can be applied. Let K_0 be the initial kinetic energy of an ion in the drift region, q the charge of the ion, V_L the potential applied to the lens electrode, and K_f the final energy of the ion as it enters a lens. Then,

$$K_f = K_o - qV_L \tag{5.1a}$$

which can be rewritten in terms of velocities as

$$\frac{1}{2}mv_{xf} + \frac{1}{2}mv_{yf} = \frac{1}{2}mv_{x0} + \frac{1}{2}mv_{y0} - qV_L.$$
(5.1b)

Since there are no radial forces in the macroscopic domain, $v_{y0} = v_{yf}$ and we can write

$$\frac{1}{2}mv_{xf} = \frac{1}{2}mv_{x0} - qV_L \tag{5.1c}$$

which can be rearranged to an equation for v_{xf} in terms of v_{x0} as the following

$$v_{xf} = \sqrt{v_{x0}^2 - \frac{2qV_L}{m}}.$$
 (5.1d)

By defining r_1 as the distance that the ion travels in the radial direction before entering a lens on the axis of symmetry and $t = r_I/v_y$ the corresponding travel time, we can also write a kinematic equation for v_{xf} with the goal of eliminating v_{xf} as a variable

$$v_{xf} = v_{x0} + a_x t \tag{5.2a}$$

where a_x is the acceleration in the axial direction due to the lens potential, given by

$$a_{x} = \frac{F_{x}}{m} = \frac{-q|E|}{m} = -\frac{qV_{L}}{d_{ML}m}.$$
(5.3)

Then,

$$v_{xf} = v_{x0} - \frac{qV_L r_1}{d_{ML} m v_{\gamma}}$$
(5.2b)

and v_{xf} can then be eliminated by equating the rearranged energy balance (5.1d) to the rearranged kinematic equation (5.2b) as

$$\sqrt{v_{x0}^2 - \frac{2qV_L}{m}} = v_{x0} - \frac{qV_L r_1}{d_{ML}mv_y}.$$
(5.4a)

However, r_1 is at this point unknown. Geometrically, r_1 can be written in terms of the radial distance from the axis of symmetry that the ion is created r_s , the source-to-mesh spacing d_{SM} , and θ_1 as

$$r_1 = r_s - d_{SM} \tan \theta_1. \tag{5.5}$$

At this point, it also becomes more convenient to rewrite velocity terms which are not yet known in terms of θ_1 using the relations

$$v_{x0} = \sqrt{\frac{2K_0}{m}} \cos \theta_1 \tag{5.6a}$$

and
$$v_y = v_{y0} = \sqrt{\frac{2K_0}{m}} \sin \theta_1$$
 (5.6b)

which yield

$$\sqrt{\frac{2K_0}{m}\cos^2\theta_1 - \frac{2qV_L}{m}} = \sqrt{\frac{2K_0}{m}\cos\theta_1 - \frac{qV_L(r_s - d_{SM}\tan\theta_1)}{d_{ML}m\sqrt{\frac{2K_0}{m}}\sin\theta_1}}.$$
(5.4b)

Canceling out *m* yields

$$\sqrt{2K_0 \cos^2 \theta_1 - 2qV_L} = \sqrt{2K_0} \cos \theta_1 - \frac{qV_L(r_s - d_{SM} \tan \theta_1)}{d_{ML} \sqrt{2K_0} \sin \theta_1}$$
(5.4c)

or, in terms of electron volts with $K_{eV} = K_0/q$,

$$2d_{ML}\sin\theta_1\left(\sqrt{K_{ev}^2\cos^2\theta_1 - K_{eV}V_L} - K_{eV}\cos\theta_1\right) + V_L(r_s - d_{SM}\tan\theta_1) = 0 \quad (5.4d)$$

which yields an equation that can be solved for θ_1 numerically given the ion energy K_{eV} , the lens focusing potential V_L , the source-to-mesh spacing d_{SM} , the mesh-to-lens spacing d_{ML} , and the radial distance from the axis of symmetry that an ion leaves the source r_s .

The angle can then be obtained from v_{xf} and v_y through the relationship

$$\theta_2 = \tan^{-1} \frac{v_y}{v_{xf}} \tag{5.7a}$$

and by substituting (5.6b) for v_y and the left side of (5.4b) for v_{xf} ,

$$\theta_{2} = \tan^{-1} \left(\frac{\sqrt{\frac{2K_{0}}{m}} \sin \theta_{1}}{\sqrt{\frac{2K_{0}}{m} \cos^{2} \theta_{1} - \frac{2qV_{L}}{m}}} \right) = \tan^{-1} \left(\frac{\sqrt{K_{0}} \sin \theta_{1}}{\sqrt{K_{0} \cos^{2} \theta_{1} - qV_{L}}} \right)$$
(5.7b)

and rewriting in units of electron volts,

$$\theta_2 = \tan^{-1} \left(\frac{\sqrt{K_{eV}} \sin \theta_1}{\sqrt{K_{eV} \cos^2 \theta_1 - V_L}} \right)$$
(5.7c)

which gives an expression for θ_2 in terms of θ_1 .

The algorithm first generates a random sample of ions with kinetic energies K_{eV} given by a Gaussian fit of the ion energy distribution measured via RFEA. The ions are placed at random starting positions r_s between the beam axis and the specified radius of the source aperture, R_S . V_L , d_{SM} , d_{ML} , are needed to solve Equation (5.4d) for θ_1 , which is then substituted to solve for θ_2 in Equation (5.7c). Ion kinetic energies at the start of the SIMION domain are scaled to the proper value assuming a uniform electric field since the SIMION simulation domain begins several microns away from the top of the lens. Each ion is assigned a calculated angle, kinetic energy, and a randomized radial starting position from the axis of symmetry of a single lens in the SIMION domain and the properties are written to a SIMION .fly2 file.

5.1.2. SIMION Simulation Domain

SIMION is an ion optics simulator which uses the finite-difference method to calculate a potential surface from a specified geometry with associated potentials. Ions are assigned a starting position, kinetic energy, and initial direction and their trajectories are tracked throughout the potential surface. In the SIMION lens focusing simulation, ions are deflected by spatially varying electric fields and converge to a focus at the base of the lens, which represents the grounded and conductive substrate surface. An example of the simulation geometry is shown in Fig. 5.2 below and consists of a single lens in cylindrically symmetric coordinates with the space 3 μ m in front of the lens opening, up to the substrate surface, which is separated from the lens electrode by a distance equal to the dielectric thickness. The substrate surface is set to ground potential and the lens electrode is set to the focusing voltage, while the potential at the entrance to the domain is found by assuming a linearly decreasing potential from the grounded grid 1.6 cm away from the substrate surface to the entrance of the domain. The ions enter the simulation domain with a kinetic energy and angular spread found by solving for the axial and radial velocities considering conservation of energy and the deceleration of the ions from the grounded grid to the domain entrance. The starting positions, kinetic energies, and directions of the ions were generated via a Python script which implemented the analytical solution of the macroscopic model and calls SIMION from the command line. 70 eV peak ion energy with a 3.5 eV FWHM Gaussian distribution were used as initial conditions, representing typical experimental conditions. The radial positions of the ions are recorded as they reach the plane of the substrate surface, and

the FWHM of the spatial distribution of the ions is taken as the expected feature size from simulation. Typical wall times were 30 seconds per run for 30,000 ions simulated using an Intel Core i5-6200U 4-core processor with 2.30 GHz clock speed.



Fig. 5.2: Schematic of SIMION lens simulation domain, with the domain entrance on the left and the substrate surface on the right. The axis of symmetry is shown in red and example ion trajectory lines are shown as black curves.

5.2. Simulation Results

5.2.1. Overview of Aberrations

Two types of aberrations analogous to conventional optics are inherent to the ion optics of nanopantography: spherical or geometrical aberrations from the curvature of the lens geometry and chromatic aberrations from the spread of the ion energy distribution. To find out the effect of these aberrations, simulations were conducted on a 1 μ m lens diameter geometry with varying focusing voltage under four different aberration conditions. The ion beamlets were simulated as a monoenergetic collimated

beam, a monoenergetic beam with angular distribution due to the finite source size, a collimated beam with a Gaussian energy distribution, and a beam with both an angular distribution and energy distribution. The results of this simulation are shown in Figure 5.3.



Figure 5.3: SIMION simulations showing the effect of aberrations for a 1 μ m diameter, 1 μ m dielectric thickness lens. The Ar⁺ ion beam has a peak energy of 70 eV and a FWHM of 3.5 eV for the simulations including ion energy distribution.

With a monoenergetic and parallel beam, the minimum spot size ions can be focused to has a FWHM of 3.5 nm. This size is finite due to the curvature of the potential surface of the lens causing ions closer to the edge of the lens opening to be deflected a

much larger angle than ions entering the lens closer to the central axis of the lens, analogous to spherical aberrations in light optics. Generally in ion optical systems, lenses are constructed such that the diameter of the beam is small compared to the diameter of the lens and ions trajectories can be considered paraxial [139]. The focal length of a paraxial ion lens can be described by the equation derived by Davisson and Calbick as

$$f = \frac{4V}{E_d - E_u} \tag{5.8}$$

where V is the ion kinetic energy, E_d is the downstream electric field strength, and E_d is the upstream electric field strength [80,140–142]. However, in nanopantography the diameter of each ion beamlet that is focused by an individual lens is always equal to the diameter of the lens opening since the broad-area collimated ion beam illuminates the entire substrate surface. To minimize spherical aberrations, the lens must be constructed such lens diameter is much smaller than the dielectric thickness so that ions entering the lens are deflected much smaller angles. This has the additional benefit of being able to fit higher pattern density onto a lens array and therefore the substrate surface, which may be desirable in certain applications such as patterning of nanohole arrays. However, decreasing the lens diameter also decreases the ion flux entering each lens, resulting in a decrease in etching rate and longer processing times. Alternatively, additional electrodes can be placed inside of the dielectric layer analogous to the use of multiple spherical lenses and mirrors in conventional optics to correct for spherical aberrations. This would add complexity to the lens array fabrication process, electrical connections to the sample stage, and add additional process variables to explore, but this approach is widely used in state-of-the-art ion optical systems.

The ion angular distribution due to the finite source size has the most significant effect on minimum feature size, which increases from 3.5 nm at optimum focus to 19 nm for a monoenergetic beam and 25 nm for a beam with an ion energy distribution. The addition of ion energy spread to the model increases the minimum feature size to 5 nm but has the added beneficial effect of making minimum feature size less sensitive to focusing voltage. This is because a perfectly monoenergetic beam quickly becomes defocused as the lens potential deviates from the optimum focusing voltage. For a distribution of ion energies, lower energy ions are rejected from entering the lens as focusing voltage is increased, which simultaneously raises the optimum focusing potential since higher energy ions require a higher potential for optimum focus.

Since the range of ion energies that is able to pass through a lens is narrowed by increasing the focusing voltage, the minimum feature size itself may be less sensitive to the FWHM of the ion energy distribution. Figure 5.4 shows a simulation where the FWHM of the ion energy distribution was varied from 0 (monoenergetic ions) to 9 eV. The yellow region highlights the range where feature size is within 20% of the optimum feature size at 3 eV FWHM, which corresponds to the narrowest energy distribution achieved so far in the current nanopantography system. The smallest feature size at 1 eV is still within 20% of the smallest feature size at 3 eV. Even as the energy distribution widens to 6 eV and 9 eV, the smallest feature size achieved is equal to the smallest at 3 eV as long as focusing voltage is increased.



Figure 5.4: Focusing curves for 1 µm lenses and 70 eV ions with FWHM of the IED varying from 0 (monoenergetic ions) to 9 eV. The yellow region highlights the range where feature size is within 20% of the optimum feature size at 3 eV FWHM.

While it may be tempting to use the highest possible focusing voltage to narrow the ion energy distribution, the spread of the ion energy distribution should still be minimized since the flux of ions reaching the surface is simultaneously reduced, resulting in slower etching rate and longer etching times. Ions with energies lower than the focusing voltage will be rejected from entering the lens and instead will be reflected back to the grounded plate. Since the ion energy distribution is approximately Gaussian [77], it can be estimated that 65% of ions have energy above the focusing voltage at 3 eV versus 28% and 30% for 6 eV and 9 eV assuming optimal focusing voltages of 69.5, 71.5, and 72 V, respectively. Simulation results in Figure 5.5 confirm that the percent of ions that can pass through the lens follows a Gaussian probability distribution with the same center and FWHM as the ion energy distribution. Additionally, the shape of the ion radial position distributions contributes to the actual feature size observed experimentally. The position distribution tends to deviate from a Gaussian at optimal focus and the true shape at the substrate surface for a given FWHM is not unique, necessitating additional metrics to decide the optimal focusing voltage. Generally, using the lowest focusing voltage near the feature size minima will produce the sharpest contrast and allow the highest flux for etching the substrate. Section 5.3.2 provides extensive discussion regarding optimizing the shape and contrast of the position distribution in determining the focusing voltage that will result in the smallest feature size.



Figure 5.5: Percentage of ions that can pass through the lens and reach the substrate surface versus focusing voltage for a 70 eV Ar⁺ ion beam with 3 eV FWHM. Expected feature size is also shown.

5.2.2. Effect of System Geometry

The three types of aberrations in the system have physical causes which can be minimized by adjusting system parameters. The ion energy distribution can be controlled through plasma properties, collisions in the plasma sheath, and collisions in the millitorr pressure region downstream of the source. However, these phenomena are not included as part of the model and only the effect of directly manipulating the ion energy and FWHM as a parameter can be studied. Spherical aberrations are a property of the fields that form at the lens openings and are a natural candidate for modeling in SIMION, as will be shown in Section 5.2.3. The ion angular distribution appears to have the largest effect on feature size when the effects of various aberrations were isolated and is part of the model both analytically and as part of the numerical simulation in SIMION.

To estimate the scaling of the angles in the model, Equation (5.4d) can be solved for θ_1 assuming a small angle such that $\sin \theta_1 \approx \theta_1$ and $\cos \theta_1 \approx 1$ since any ion that makes it to the sample stage must pass through a 1 cm wide aperture at the end of the 60 cm drift region, which only allows ions from the source with angles less than 0.48° measured from the beam axis. Equation (5.4d) then becomes

$$\theta_1 \approx \frac{V_L r_s}{V_L d_{SM} + 2d_{ML}(K_{eV} - \sqrt{K_{eV}(K_{eV} - V_L)})}$$
(5.4e)

which shows that θ_1 is proportional to the radial displacement from the beam axis and inversely proportional to the source-to-mesh spacing and the mesh-to-lens spacing. Both terms in the denominator are the same order of magnitude since the optimum focusing voltage is usually within 20% of the ion energy. Similarly, θ_2 is expected to increase with the source size and decrease with the axial length of the system though the scaling is complex since θ_2 does not satisfy the small angle approximation and is related to θ_1 by Equation (5.7c). Intuitively, we expect that the ion angular distribution will be reduced by a smaller source aperture and a larger distance between the source and the sample, and the system was previously redesigned on those principles by Tian. The effect on ion angular distribution is difficult to experimentally quantify since ion angular distributions cannot be easily measured and varying the source-to-mesh spacing requires time-consuming and expensive steps including machining new parts and reconstruction of the system. Simulations are the most practical tool to study the variation of system geometry and were conducted by varying the diameter of the source aperture, source-to-mesh spacing, and mesh-to-lens spacing.

Figure 5.6 shows expected feature size versus focusing voltage for various source-to-mesh spacings. The current nanopantography system uses a 60 cm spacing, which was increased from 30 cm in the first-generation nanopantography system used by Xu [79]. Based on geometry, the maximum admittance angle at the aperture on the grounded plate decreases by a factor of 2 from 0.95° to 0.48°. The maximum θ_1 given by Equation (5.4d) also decreases by a factor of 2 from 0.44° degrees to 0.22° for 100 eV ions focused at 97 V. The minimum feature size estimated by simulation decreases from 40 nm to approximately 25 nm. Increasing the source-to-mesh distance from 60 cm to 120 and 180 cm further reduces the minimum feature size to 18 nm and 13 nm, respectively, which is approximately a 28% reduction in feature size for every 60 cm increase. Realistically, the source-to-mesh distance cannot be increased indefinitely since the ion current was found to be inversely proportional to the square of the distance away from the source, so doubling the length of the system will result in one-fourth of the ion flux at the sample and feature minimization will have to be balanced with processing times [77]. At these lengths, the nanopantography system becomes very long, requiring significant redesign and construction to experimentally confirm these effects.



Figure 5.6: Expected feature size vs. focusing voltage for varying source-to-mesh distances.

While the source-to-mesh distance in the system cannot be easily changed, the spacing from the mesh of the grounded plate can be easily increased by adding additional ceramic standoffs to the sample holder and is worth exploring with simulations. Figure 5.7 shows expected feature size versus focusing voltage for a mesh-to-lens spacing of 0.8 cm to 6.4 cm while keeping the total length of the system constant. As expected, the minimum feature size weakly decreases as the spacing is increased, only a few percent over the spacing range studied. From Equations (5.7c) and (5.4e), increasing d_{ML} alone should decrease θ_1 , which decreases θ_2 by decreasing the sine in

the numerator. However, the effect is not as strong as doubling the source-to-mesh distance (i.e. increasing the total system length) since increasing the mesh-to-lens spacing reduces the source-to-mesh spacing which results in an increase in θ_1 and therefore θ_2 . Additionally, while the denominator of Equation (5.4e) is proportional to both spacings, d_{SM} is multiplied by V_L whereas d_{ML} is multiplied by an expression that is always less than V_L except in the case that V_L is equal to the ion energy, so that reducing d_{SM} results in an increase of θ_1 while keeping the total system length constant. Since d_{SM} is much larger than d_{ML} , there exists some optimal location of placing d_{ML} that minimizes the angular distribution. However, this location is difficult to determine since the angular distributions depend on the ion energy and optimal focusing voltage, which in turn depends on the system geometry as well as lens geometry. Since the minimum feature size does not appear to be particularly sensitive to the source-to-mesh spacing on the centimeter scale, it is satisfactory to keep the current spacing of 1.6 cm. Experiments should be conducted to vary the distance between the grounded plate and verify the observations from simulation.



Figure 5.7: Expected feature size vs. focusing voltage for varying mesh-to-lens distances keeping the total system length constant.

The final system geometry parameter that can be studied in the model is the diameter of the aperture on the ion beam source. Classical objects suggests that the source size is related to the object size and a smaller object will product a smaller image. Tian also suggested that narrowing the aperture should result in a narrower ion angular distribution, and the nanopantography system was modified from 11.4 mm diameter to 5 mm which was kept in experimental studies by Chen and in this dissertation [78,80]. Additionally, a larger aperture was found in SIMION simulations by Tian to result in a loss of ion current at the sample due to increase buildup of space-charge, though it is

questionable if this would be observed since Chen demonstrated that present method of generating an ion beam results in a sufficiently space-charge neutralized beam [77,80].

Figure 5.8 shows expected feature size versus focusing voltage for a point source and varying source diameters from 3 mm to 20 mm. While feature size is decreased by reducing the size of the source aperture from 20 mm diameter to 10 mm, no further reduction in feature size is observed from additional reduction of the aperture diameter. As the size of the source aperture decreases, the maximum admittance angle of an ion exiting from the edge of the source aperture and transiting through the opposite edge in the grounded plate on the sample stage decreases, which is calculated from

$$\theta_{max} = \arctan \frac{R_s + r_{plate}}{d_{SM}}$$
(5.9)

where r_{plate} is the radius of the aperture of the grounded plate, equal to 5 mm. Reducing the source from 20 mm to 3 mm results in a reduction of the maximum admittance angle from 2.4° to 0.8° and a corresponding reduction of the minimum feature size from 50 nm to 23 nm. As seen earlier in Figure 5.3, the ion angular distribution appears to be the most significant limitation on the resolution of nanopantography and reducing the diameter of the source aperture to an ideal point source can theoretically result in nanometer-scale features in the 1 µm by 1µm lens geometry for removable SU-8 lenses. Unfortunately, reducing the diameter of the source aperture also results in a significant reduction of the ion flux available to etch the sample scaling with $1/d^2$. While a 3 mm diameter source may still be able to provide enough flux for etching with reasonable throughput, further reduction to 1 mm and even smaller may increase etching time an order of magnitude or more from minutes to hours. Still, this may be worth pursuing if minimizing feature size is key and other steps can be used to increase throughput such as highly selective anisotropic etching in a second plasma. Any method that will reduce the ion angular distribution is likely to result in a significant increase in resolution for nanopantography.



Figure 5.8: FWHM vs. focusing voltage for varying source diameters.

5.2.3. Effect of Lens Geometry

Simulations were conducted varying the diameter of the lens opening while keeping a fixed dielectric thickness of 1 μ m. As the lens aspect ratio narrows, the

minimum expected feature size at the optimum focusing voltage decreases 33% from 24 nm at a 1:1 length to diameter ratio lens to 16 nm for a 3.3:1 aspect ratio lens. This is due to minimizing the effect of spherical aberrations, since a lens with a larger length to diameter ratio will require smaller angles to deflect ions to the focal point. However, decreasing the diameter of the lens opening reduces the ion flux reaching the substrate surface, requiring longer etch times. This is counterbalanced by the fact that lower focusing voltages are required to focus the lens when the aspect ratio is narrower, allowing lower energy ions to reach the substrate surface and increasing the ion flux at the substrate surface. Narrowing the lens does not appear to influence the sensitivity to focusing voltage, as the 1:1, 1.7:1, and 3.3:1 aspect ratio lenses all have expected feature sizes within 20% of their minimum for a ± 2 V change in focusing voltage. Using a wider aspect ratio lens with diameter larger than length is not useful since expected feature size will be larger than lenses with more narrow aspect ratios and a minimum feature size is not reached even as focusing voltage is increased. Lenses with diameters smaller than the dielectric thickness are preferred to minimize feature size.



Figure 5.9: SIMION simulations showing expected feature size vs. focusing voltage for various dielectric thickness (lens length) to lens diameter ratios for 1 μm thick lenses.

5.2.4. Lens Scaling

Previously, Tian was able to improve the minimum nanopantography etched feature size from 15 nm to 3 nm by reducing lens dimensions from 1150 nm dielectric, 650 nm diameter (SEMATECH samples) to 300 nm dielectric, 230 nm diameter, resulting in a 77x size reduction of the lens opening in both cases. Current results with print-and-repeat nanopantography show a 50x size reduction of the lens diameter. Scaling down the lens size in both dimensions is likely to produce even smaller features as well as higher pattern density competitive with the resolution and throughput of EUV patterning. SIMION simulations were performed with 100 nm dielectric thickness lenses and compared to 1 μ m dielectric lenses with the same aspect ratio with results shown in Figure 5.10 below.



Figure 5.10: Simulation of 1:1 dielectric thickness to diameter ratio (left) and 2.5:1 (right) for 100 nm and 1 µm dielectric thickness with varying focusing voltage. Ar⁺ ion beam had 70 eV peak ion energy, 3.5 eV FWHM.

It is clear from these results that scaling down the size of the lens by 10x will result in smaller feature sizes by at least 10x. In fact, the true size reduction is even greater due to the smaller lens openings admitting a narrower angular distribution of ions. By estimating a 50x reduction in the lens diameter, the 1:1 aspect ratio (100 nm diameter) lenses should be able to produce a feature size of 2 nm while the 2.5:1 aspect ratio (40 nm diameter) lenses should yield 0.8 nm features. However, the print-and-repeat nanopantography lenses are limited by the dielectric strength of SU-8, which is 120 to 400 V/ μ m for high quality thin films [143]. Instead, a process was developed to fabricate conventional nanopantography lenses from SiO₂ (dielectric strength 1000 V/ μ m) which can be grown with sufficient quality to withstand the voltages required for
nanopantography. Lens diameters were varied from 50 nm to 110 nm (2.2:1 to 1:1 aspect ratio) to study the effect of lens diameter versus feature size at a fixed lens dielectric thickness and to assist in obtaining the smallest possible features. Details of this process developments were adapted from the dissertation of Tian [80].

At this feature size, imaging the etched feature becomes a major issue. Tian was able to image 3 nm holes with a SEM (Figure 5.11) by cleaving a sample after etching in the nanopantography system to obtain cross sections of lenses along the cleavage planes. This method requires an extreme level of luck to get the cleavage plane to run through the center of a hole, so it is recommended to etch a longer shape such as a trench to increase the probability of cleaving through a feature. Additionally, nanopantography can be followed by highly selective plasma etching in a Cl₂ plasma under photo-assisted etching (PAE) conditions to enhance the contrast of the etched feature so that the feature may be visible from a top-down view in SEM. Both strategies will likely need to be used to image nanometer scale etched features with thin dielectric lenses.



Figure 5.11: SEM cross sections of 3 nm holes in silicon with SiO₂ lenses on Si (230 nm diameter, 300 nm dielectric thickness) before (left) and after (right) highly selective plasma etching of Si in Cl₂ plasma. From Tian [28].

5.3. Model Limitations

5.3.1. Ion Angular Distribution

In the discussion effort to determine angles θ_1 and θ_2 , it is necessary to differentiate them from the ion angular distribution of the source, which was estimated from plasma measurements and application of the Child-Langmuir law yielding $\theta_{av} \approx 2^{\circ}$ for 100 eV Ar⁺ ions [77]. However, the ion angular distribution past the grounded plate is narrower since the ions must pass through a 1 cm wide aperture at the end of the 60 cm drift region, which only allows ions from the source with angles less than 0.48° measured from the beam axis assuming a point source and 0.95° assuming a 5 mm diameter source aperture according to Equation (5.9). The true angular distributions in the system and the lens are a function of both plasma properties and system geometry, while the present model only considers system geometry. A more complete model of the system may be able to include measured ion angular distribution, though angular distributions are also difficult to experimentally determine and requires the removal of the sample stage to allow ion beam measurements with the Faraday cup. Since the grounded plate restricts angles greater than 0.95°, narrowing the real ion angular distribution out of the source while keeping emitted ion current constant will likely result only in an increase in ion flux to the substrate unless the angular distribution can be narrower than 0.95°. However, any methods that can potentially decrease the ion angular distribution emitted from the source is worth pursuing since it was demonstrated in Sections 5.2.1 and 5.2.2 that ion angular distribution is the most significant limitation to the resolution of nanopantography.



Figure 5.12: 1 μ m lens with 70 eV Ar⁺ ions at 65-72 V lens potential with shapes of ion radial position distribution at the substrate surface in red and Gaussian fit shown in blue. Dashed lines border the FWHM.

5.3.2. Contrast and Real Feature Sizes

Both in simulation and experiment, ions strike the surface in an area larger than reported feature sizes, which are based on interpretation of position distributions, feature profile, and imaging contrast. Consequently, there is a possibility of etching away material anywhere an ion strikes.

Figure 5.12 shows the evolution of the shape of the ion position distribution at the substrate surface for a 1 μ m diameter lens with 1 μ m dielectric as focusing voltage is increased in red with Gaussian fits shown in blue. Focusing voltage, ion position FWHM at the substrate surface, and percent of ions that fall within the FWHM are shown above each profile. At focusing voltages below 95% of the ion energy, the distribution is narrower than the Gaussian fit but the image on the substrate surface is only reduced one order of magnitude smaller than the diameter of the lens. Over 76% of the ions fall within the FWHM, which is the percentage expected from a normal distribution. At focusing voltages near 95% of the ion energy, the distribution is wellfitted by a Gaussian and the feature size can be two orders of magnitude lower than the diameter of the lens. At higher focusing voltages, the feature FWHM and percentage of ions falling within the FWHM do not appear to change for this particular lens geometry and the expected feature size is similar regardless of focusing voltage. However, one thing that should be noted is that the peak of the distribution has a lower count (out of 30,000 ions simulated) as focusing voltage is increased, giving a warning that ion flux for etching at the substrate surface is small and that there might be differences in the

shape of the ion position distribution that can result in differences in feature size and profile, as discussed in the following paragraphs.

It is not necessarily possible to obtain a narrow Gaussian beam shape, and the smallest feature sizes in experimental processing will need to consider contrast and exposure times. Since different ion distribution position shapes can produce the same FWHM, another measure is needed to determine what focusing voltage is optimum and what shape will result in the smallest feature. One possible tie-breaking method is the use of the slope of the ion position distribution at the FWHM. Figure 5.13 shows the slope at the FWHM position ($r = \pm FWHM/2$ at the substrate surface) versus focusing voltage for a 70 eV ion beam with 3 eV energy FWHM and a 1 µm diameter, 1 µm dielectric lens. In total, 30,000 ions were simulated and a histogram was constructed with a bin size of 1.25 nm. The FWHM of the position distribution and percent of ions inside the FWHM are also plotted. The FWHM reaches a plateau of approximately 27 nm in the focusing voltage range between +69 V and +72 V. The percent of ions that fall within the FWHM reaches a plateau of 50% in the same voltage range, indicating that it cannot be used as a measure to select an optimal distribution shape (and therefore focusing voltage) when multiple distributions have the same FWHM. However, the slope at the FWHM reaches a maximum of 64 counts/nm at +69.5 V and varies sharply with focusing voltage. A higher slope indicates higher contrast since the number of ions falling at a position will rapidly drop off as distance is increased from the center of focus.



Figure 5.13: FWHM of the ion position distribution (black squares), percent of ions falling within the FWHM, and the slope of the distribution at the FWHM position versus focusing voltage. Slope can be used as a measure of contrast.

Another method to measure contrast is to relate the ratio of ion counts at the center of focus versus the ion count at a certain distance away from the center. An advantage to this method is if ion flux at the sample surface, etching yield, and selectivity can be determined experimentally and the model accurate predicts the ion position distribution at the sample, then feature size can be related to beam exposure time. But even if the contrast is very high, there will be some damage to the surface around the focal point. The addition of a masking layer resistant to etching by the beam ions may be necessary to produce the smallest possible features since etching has the chance of occurring anywhere an ion strikes, not just within the FWHM of the position distribution. The necessary and most optimal approach is to combine high contrast,

narrow position distributions with a highly selective mask such as SiO_2 in the case of etching of Si with an Ar^+ beam in a background of Cl_2 gas similar to the work of Tian to etch sub-3 nm features using nanopantography [28]. Simulations have predictive power, but only reaffirm what we already know: in order to achieve the smallest possible features, the ion beam source needs to be monoenergetic, but most importantly well collimated.

5.4. Summary

A multiscale model of the system was created using an analytical solution for the macroscopic ~60 cm ion drift region starting from the exit of the ion beam source and the numerical simulator SIMION for the microscopic ion focusing region starting 3 μ m away from the lens openings. Simulations were performed to study the relative importance of aberrations resulting from lens geometry, ion energy distribution, and ion angular distribution. Additional simulations were performed to optimize system geometry and lens geometry, resulting in the prioritization of the minimization of ion angular distribution and lens dimensions to ultimately achieve sub-nanometer. Finally, a method was developed to quantify image contrast to select focusing voltages that produce optimum feature sizes when several voltages appear to produce similar sizes.

Chapter 6 Patterning of Carbon-Based Materials with an Oxygen Ion Beam

One of the major goals of developing removable nanopantography lenses is to etch different materials for novel applications such as graphene nanohole arrays, which do not currently have a high-throughput method of patterning arbitrary shapes on the sub-100 nm scale and typically relies on ion beam lithography, dip-pen nanolithography, block copolymer self-assembly [85,114,144]. While or nanopantography lenses can be manufactured on various substrates, significant process development must be conducted to select suitable materials for deposition, patterning lens openings, and lens dielectric. Efforts are better concentrated on developing reusable membrane-based lenses to pattern graphene and other arbitrary substrates on this scale using a suitable ion beam source for etching. Existing work on plasma-assisted etching of graphene has used hydrogen, oxygen, H₂O₂, and even argon sputtering [114,117,145] and atomic layer etching with low energy O_2^+/O^+ ion beam followed by exposure to a low energy 11.2 eV Ar⁺ ion beam [121,122]. In this work, patterning of graphene and other carbon-containing materials was conducted using an ion beam generated by an oxygen plasma generated in the nanopantography source.

6.1. Oxygen Beam Diagnostics

The method of generating a self-neutralized nearly-monoenergetic ion beam from a pulsed plasma with synchronous DC bias in the afterglow has been studied extensively for argon plasmas and briefly investigated for other noble gases [71,73,74,146,77]. In these systems, the main species are neutral atoms, monatomic positive ions, electrons, and excited and metastable states. The resulting ion beam is space-charge self-neutralized due to the emission of positive ions and electrons during the unbiased period of the early afterglow, which form a neutralizing volume in the downstream region near the exit of the source. Presently, this method has not yet been applied to electronegative plasmas, which contain negative ions that suppress the bulk electron density to maintain quasi-neutrality with positive ions. While negative ions can potentially exit the source during the afterglow of the pulsing period, ion-ion plasma formation only occurs late in the afterglow [147], coinciding with the typical time that positive ions are extracted by synchronous DC bias on the boundary electrode. The strong +70 to 100 V DC boundary bias also attracts negative ions, preventing them from leaving the source and causing perturbations to the acceleration potential felt by positive ions. The possible effects of negative ions on extraction, self-neutralization, and ion energy distribution are numerous and must be thoroughly investigated to find optimum experimental conditions for oxygen ion beam etching.

6.1.1. Experimental Methods for Oxygen Ion Beam Diagnostics

Experiments were conducted using the system and methodology detailed in Chapter 3, with modifications listed below. Deviations from these conditions are listed in the appropriate section. Pure O₂ gas was admitted into the source at 5.4 sccm in order to maintain a source pressure of 12 mTorr, which needed to be higher than the pressure of Ar plasma in order to maintain stability during pulsed operation. The plasma was operated at 800 W peak RF power at 13.56 MHz, pulsed at 10 kHz and 65% duty cycle which was determined to be the minimum duty cycle and power off time that the oxygen plasma could be pulsed while still reigniting. A 100 V DC bias (V_{bias}) voltage was applied to the boundary electrode 15 μ s into the afterglow ($t = 80 \ \mu$ s), lasting 15 μ s, which was shortened from the Ar⁺ ion beam condition to fit into the 100 μ s period cycle. The retarding field energy analyzer (RFEA) described in Chapter 3 was used to measure ion current and ion energy distribution during diagnostic experiments and before each etching experiment. Typical ion currents were 30-60 nA measured at the 1 inch diameter current collection plate of the RFEA, 80 cm downstream of the extraction grid.



Figure 6.1: Schematic of the pulsed plasma power and bias sequences for oxygen beam experiments.

6.1.2. Determination of Oxygen Ion Beam Composition via Time-of-Flight Mass Spectrometry

In an oxygen plasma, multiple positive ion species can be generated. O_2^+ and O^+ are expected to dominate with few O_3^+ and O_4^+ ions present for low-temperature glowdischarge plasmas [148,149]. While either 100 eV O^+ or O_2^+ ions may participate in etching, understanding the relative distribution may provide useful information especially if etching yields are different for the two ions. Since the ions have different masses but are both accelerated to 100 eV by the boundary bias, a time-resolved measurement of ion current should be able to show the relative distribution of ions, similar to the method of time-of-flight mass spectrometry. The speed of an ion is given by

$$v = \sqrt{\frac{2K_e}{m}}$$
(6.1)

where K_e is the kinetic energy and *m* is the mass of the ion. The expected time of flight *t* of an ion traveling a distance *d* is given by

$$t = \frac{d}{\sqrt{\frac{2K_e}{m}}} = 71.98 \, d \sqrt{\frac{m_{amu}}{K_{eV}}} \, [\mu s] \tag{6.2}$$

where m_{amu} is the atomic mass in daltons, K_{ev} is the kinetic energy in electron volts, and d is the distance in meters between the aperture of the source and the current collector plate of the RFEA, measured to be 0.92 cm. For 100 eV O⁺ and O₂⁺ ions the expected times of flight are 25.9 µs and 36.6 µs, respectively. However, there is a distribution of flight times due to both the width of the ion energy distribution as well as the spatial distribution of ions in the source and the ion response time to the accelerating boundary bias. These distributions, combined with delays caused by instrumentation response time, will cause a delay between the expected time of flight and the observed peak ion current. To estimate the delay, the ion energy distribution and time-resolved ion current for an Ar⁺ ion beam was measured, shown in Figure 6.2. The peak ion energy was 96.9 eV, which corresponded to an expected flight time of 42.5 µs. However, the time-resolved ion current shows that the peak corresponding to the 96.9 eV ions actually occurs at 57 µs, a 14.5 µs delay which will be assumed to be the same delay for the following analysis of an ion beam generated from an O₂ plasma. A smaller peak is

detected 50 μ s after plasma power is turned on, which corresponds to low energy (10-15 eV) ions generated during the active glow from the previous cycle arriving at the current collector plate.



Figure 6.2: Time-resolved ion current for a 96.8 eV peak energy, 6.8 eV FWHM Ar⁺ ion beam generated by applying +98.2 V, 15 μs synchronous boundary bias 20 μs into the afterglow of a 10 kHz, 20% duty cycle pulsed plasma.



Figure 6.3: Ion energy distribution for an ion beam generated from pure O₂ plasma at 800 W, 65% duty cycle, and +98.2 V boundary bias applied 15 μs after plasma is turned off for a duration of 15 μs.

The ion energy distribution for an ion beam generated from a 15 mTorr O₂ plasma with a 15 µs duration, +98.2 V synchronous DC bias applied 15 µs after plasma power is turned off is shown in Figure 6.3. The peak ion energy is 95.5 eV, which corresponds to flight times of 27.1 µs and 38.3 µs for O⁺ and O₂⁺, respectively. The main ion energy peak has a high-energy tail extending up to 120 eV, indicating that the plasma potential has not fully dropped to zero during the early period of boundary bias. For 5 mTorr Ar plasma in the source, T_e was found to drop from 4.8 eV at the end of power-on to 0.4 eV 15 µs after the beginning of power-off [77]. Langmuir probe 106

characterization of the nanopantography ion beam source under O₂ plasma was unavailable, but time-resolved Langmuir probe measurements by Lee for a 1400 W, 5 kHz, 50% duty cycle pulsed O_2 ICP show that electron temperature drops from 2.3 eV during the powered period to 0.8 eV 15 µs into the afterglow. At 30 µs into the afterglow, the electron temperature reaches 0.6 eV, where it remains until the end of the afterglow [150]. Additional broader and less intense peaks appear at 36, 55, and 77 eV which correspond to species produced during the 65 µs active glow. Charles and Boswell found that the high peak is produced by transient instabilities at the initiation of plasma breakdown, the medium energy peak is produced by the powered period, and the low energy peak is produced by extraction of ions in the afterglow [151]. Midha and Economou observed that a large spike in T_e occurs at the beginning of the active glow of a pulsed electronegative plasma if all the electrons are lost in the afterglow and an ion-ion plasma was formed [152], which would lead to a spike in V_p and the high energy 77 eV peak. These broad energy peaks created in the active glow are likely to appear in the time-resolved ion current measurements as a constant background of ions since the duration of powered plasma is longer than the duration of the afterglow.



Figure 6.4: Time-resolved ion current for a 95.5 eV peak energy, 6.4 eV FWHM O_2^+ ion beam generated by applying +98.2 V, 15 µs synchronous boundary bias 15 µs into the afterglow of a 10 kHz, 65% duty cycle pulsed O_2 plasma.

Figure 6.4 shows the time-resolved current corresponding to the IED in Figure 6.3. The main current peak appears 52 μ s after application of bias (32 and -68 μ s on the x-axis), which corresponds to the expected flight time of 95.5 eV O₂⁺ ions assuming the same 14.5 μ s delay as for Ar⁺ ions. Approximating the time-resolved current peak as a triangle with a base of 50% of the cycle, the 90 nA peak in the time-resolved measurement yields a time-averaged current of 22.5 nA which is consistent with the current measured as the area under the peak in the time-averaged IED measurements. The base of this main time-resolved peak spans roughly 50 μ s despite a bias duration of 108

only 15 μ s, with an increase in current indicating the start of the peak at 33 μ s after the bias is turned on and lasting until 80 µs after bias is turned on. For comparison, the main Ar+ ion peak spanned 40 μ s for the same bias duration, and the additional width of the O_2 peak may be due to additional species with either different mass or kinetic energy. The main peak has a slight shoulder at earlier arrival times and a slight tail at later arrival times. The earlier shoulder peaks at 39 µs after application of bias (19 and -81 µs on the x-axis), corresponding to 95.5 eV or higher energy O^+ ions which are expected to peak at 41.5 μ s after application of bias or earlier. The shoulder is not likely to be caused by higher energy O_2^+ ions, since even 120 eV O_2^+ ions will peak at 48.7 µs after bias on, while 120 eV O⁺ ions can peak at 38.6 µs after bias is turned on. Although it is difficult to estimate the ratio of O_2^+ ions to O^+ ions, experimental studies of O_2 plasma generally indicate low dissociation, with O^+ only making up about 1-2% of O_2^+ density [153]. The identity of the later tail is more difficult to elucidate since it may simply be caused by lagging O_2^+ ions as lagging Ar^+ ions also contribute to a tail in the Ar^+ time-resolved current measurements in Figure 6.2. Another possibility is the production of 70 to 80 eV O_2^+ ions produced during the initiation of plasma breakdown at the start of the powered plasma period. Assuming a peak energy of 77.6 eV, these ions are expected to generate a peak at 57 μ s after the plasma is turned on (assuming the same 14.5 μ s peak delay observed for Ar^+ ions), which matches with the tail. The low energy 30-40 eV O_2^+ ions exiting the source in the early afterglow of the plasma also arrive around 77 μ s after plasma is turned off (42 μ s on the x-axis of Figure 6.4), overlapping with the same region as the tail. The ions generated during the 65 µs powered period of plasma span 40 to 70 eV in ion energy and likely form the 13 nA baseline seen throughout the entire 100 μ s plasma cycle since their energy distribution is broad and they are generated throughout most of the cycle. In comparison to Ar beam measurements in Figure 6.2, Ar⁺ ions generated in the shorter 20 μ s powered plasma period form a short current peak that does not overlap with the high energy Ar⁺ current peak, and the baseline for the time resolved current measurements are nearly zero.

In summary, the majority of beam ions generated by the synchronous DC bias applied during the afterglow of the plasma appear to be high energy O_2^+ ions, with some O^+ ions present with the same energy appearing slightly earlier as a shoulder overlapping with the detection of O_2^+ ions. The peak time-resolved current detected is 90 nA, which corresponds to roughly 21 nA of time-averaged high energy O_2^+ current. The tail is most likely a result of delays caused by the spatial distribution of ions in the source resulting in broadening of the main peak, since a tail is also observed for Ar⁺ ions. Ions generated during the 65 µs powered plasma period form the observed 13 nA baseline.

6.1.3. Effect of Pressure

Minimization of the width of the ion energy distribution is important in achieving the smallest possible feature sizes, as was detailed via simulations in Chapter 5. Previous work on characterizing Ar^+ ion beams from the nanopantography source showed that the shape of the ion energy distribution was dependent on pressure, with the narrowest IEDs occurring at lower pressure due to highly forward scattering of ions

in the beam as they pass through the region of relatively high pressure of the order of a mTorr, compared to the differentially pumped drift region at 10^{-7} Torr pressure, in the first few cm on the downstream side of the grid [77]. Lower pressure also generally increased high energy Ar⁺ ion current at the sample as long as pressure was high enough to maximize source plasma density, since low pressure minimizes current loss from collisional scattering along the beam path by maximizing mean free path.



Figure 6.5: Ion energy distributions measured with the RFEA under different pressures (8 - 20 mTorr) of the ICP source. Otherwise, base conditions defined in Section 6.1.1 were used.

Figure 6.5 shows ion energy distributions measured by the RFEA for an oxygen plasma as a function of pressure in the plasma source. The minimum source pressure

required to sustain a stable O_2 plasma in the source geometry and operating conditions was roughly 7.5 mTorr, more than double the minimum pressure at which an Ar plasma could be operated. However, the ion current, peak energy of the IED, and FWHM of the IED seem to be nearly independent of pressure in the entire 8 to 20 mTorr pressure range studied. The high energy ion beam current (found by integrating the area under a Gaussian fit to the IED) remained at 21 nA despite the increasing probability for charge exchange collisions in the first few cm downstream of the grid and increased gas pressure along the beam path. The peak ion energy showed a slight monotonic increase from 97.1 eV at 8 mTorr and increased to 97.3 eV at 20 mTorr, whereas peak ion energy actually decreased with pressure for an Ar^+ beam. While T_e decreases with pressure in a continuous O_2 plasma, the effect is less pronounced in the afterglow since T_e has already decayed under 1 eV in the 15 µs that elapses after power is turned off [150,154] and the decrease of 0.2 eV in the peak ion energy may be simply due to error given the limits of the RFEA and peak fitting method. The FWHM of the IED remained at 7.3 eV from 8 mTorr to 15 mTorr, but jumped to 7.9 eV at 20 mTorr, making it the only trend to change significantly with pressure.

As the ion current and energy spread (21 nA, 7.3 eV FWHM) are already dramatically less optimal for etching compared to Ar ion beam conditions (200 nA, 4 eV FWHM), other processes that are not strongly pressure dependent seem to dominate, reducing ion current and increasing the energy spread. The electron density in an oxygen plasma, roughly equal to the plasma density at lower pressures (<50 mTorr), is lower than an argon plasma under similar operating conditions, accounting for at least a factor

of 2 and up to a factor of 10 in the reduction of positive ion beam current [149,155– 157]. Increasing the pressure may have the added effect of increasing plasma density in the operating regime, balancing any loss in ion current loss due to increasing downstream collisions [154,158,159]. However, the actual magnitude of plasma density effects from pressure changes must be confirmed for the specific operating conditions and geometry of the nanopantography system. The role of negative ions needs to be further investigated, since they play a significant role in the afterglow of pulsed electronegative plasmas and may interfere with ion extraction and the formation of a self-neutralizing downstream plasma. Increasing pressure can also cause increases the electronegativity of the plasma and therefore the importance of reactions including negative ions such as associative detachment which generates electrons in the afterglow [150]. Further time-resolved oxygen plasma diagnostics are necessary to understand the behavior of negative ions and fully explain pressure effects.

6.1.4. Effect of Bias Delay

The strategy for maximizing ion current with an Ar⁺ plasma involves applying bias with a long enough delay to allow the electron temperature to nearly reach zero (minimizing energy spread), balancing this with the reduction in positive ion density in the source further into the afterglow. Furthermore, measurements for an Ar+ plasma showed that ion current was lower when bias was applied too soon in the afterglow, possibly due to not enough time elapsing for ions and electrons to diffuse across the extraction grid and form a downstream neutralizing low-temperature plasma. Optimal ion current and IEDs were obtained when the start of bias occurred 15-25 μ s into the afterglow, which was used as a starting point for subsequent O₂⁺ beam patterning experiments described later in this chapter. However, this section presents diagnostics performed after-the-fact to understand the dynamics of positive ion extraction in the afterglow of an O₂ plasma.



Figure 6.6: Ion energy distributions measured with the RFEA with different bias delays applied $1-20 \,\mu s$ after plasma-off (corresponding to $66-85 \,\mu s$ in the cycle). Bias duration remained fixed at 15 μs .

Figure 6.4 shows ion energy distributions measured by the RFEA for an oxygen plasma as a function of boundary bias application time. Plasma is turned off at 65 μ s in the 100 μ s cycle, though boundary bias cannot be applied at exactly 65 μ s or during the

plasma on period due to current saturation of the amplifier. This also limits the maximum bias-on time to 85 μ s (20 μ s into the afterglow) at a fixed bias duration of 15 μ s. When bias is applied immediately in the afterglow, the beam ion current is 18 nA, which reaches a maximum of 23 nA at 10 μ s bias delay before falling by more than half to 10 nA at 20 μ s delay. The peak ion energy varies around 97 \pm 0.5 eV but jumps to 98.7 eV at 20 μ s bias delay. The FWHM starts at 5.3 eV at the beginning of the afterglow, reaching a maximum of 7.2 eV at 15 μ s bias delay. This indicates that the optimum time to apply bias is immediately in the afterglow up to 15 μ s later, whereas for Ar⁺ plasma the best time to apply bias is at least 20 μ s into the afterglow. These trends are summarized below in Figure 6.7.

The initial increase in ion current matches what was observed for an Ar^+ ion beam, suggesting that ions and electrons are exiting the source and beginning to form a space charge neutralizing plasma in the downstream region that reduces current loss [77]. Ion current decreases further as time passes since the positive ion density in the source also drops. Additionally, the escape of electrons from the source allows for the formation of an ion-ion plasma after 10 µs into the afterglow, changing the electrical properties of the plasma such that negative ions become the dominant negative charge carrier and the plasma potential is determined by the ion temperature rather than the electron temperature. Weak electric fields are able to be sustained in the plasma, which may explain the increase in the FWHM of extracted ions as bias is increased since not all ions are uniformly raised to the same potential upon application of bias. A smaller high energy peak develops as time increases into the afterglow, peaking at 110 eV at 15 µs bias delay and decaying into a tail as time into the afterglow is increased. The cause of this peak is unknown but may be related to the generation of electrons in the early afterglow due to associative detachment and their subsequent acceleration to 100 eV by attraction to the positive DC boundary bias.



Figure 6.7: Ion energy and FWHM measured with the RFEA with different bias delays applied $1-20 \,\mu s$ after plasma-off (corresponding to $66-85 \,\mu s$ in the cycle). Bias duration remained fixed at 15 μs .

In summary, many trends that were observed with an Ar^+ ion beam were not present with an O_2^+ ion beam. Ion current was found to be an order of magnitude lower than what was generated with an Ar plasma, likely due to the decreased O_2 plasma density at similar operating conditions. Pressure plays a weak role in the extracted ion 116 current and energy spread. The optimum time to apply bias appears to be immediately in the afterglow to minimize FWHM of the ion energy distribution, though extracted high energy ion flux increases as the bias delay is increased to 20 µs. Further studies of the pulsed oxygen ICP, including time-resolved Langmuir probe measurements, are needed to fully understand the plasma dynamics under the specific geometry and operating conditions of the nanopantography system. Further exploration of operating conditions such as power and pulsing frequency are recommended to increase ion current.

6.2. Patterning of PMMA with an O₂⁺ Ion Beam

Poly(methyl methacrylate) (PMMA) is a spinnable photoresist consisting only of carbon, hydrogen, and oxygen molecules, and is readily etched in oxygen plasmas, forming CO₂, CO, and water as byproducts. Proof of concept experiments were conducted using a substrate consisting of 100 nm of PMMA spun on a Si wafer and baked for 30 minutes at 180 °C. A 160 μ m thick transparency film with a 7 mm diameter circular hole punch was placed on top of the PMMA as the dielectric for a lens electrode consisting of a metal mesh with 100 μ m diameter circular holes and 60 μ m thickness. A nearly monoenergetic O₂⁺ ion beam was generated using the methods earlier in this chapter, with source pressure of 12.5 mTorr and 15 μ s long bias applied 15 μ s into the afterglow. Measurements of the IEDs yielded 30 nA/cm² ion beam current density at the sample location and 98 to 100 eV ion energies between with FWHM of 6 eV. The metal layer on top was biased with DC voltage ranging from 88 V to 96 V. The samples were exposed to the ion beam for 60 to 273 minutes.



Figure 6.8: Optical microscope images of O_2^+ beam patterns formed in PMMA at various focusing voltages and etching times. A metal mesh with 100 μ m diameter holes was used as the lens.

Table 6.1: Summary of experimental conditions and measured feature sizes for O_2^+ beam patterns formed in PMMA using a metal mesh with 100 μ m diameter holes as the lens.

Focusing Voltage (V)	Exposure Time (min)	Average Feature Size (μm)
88	273	19.1
90	50	No Feature
90	150	18.9
92	120	18.8
94	90	10.5
94	30	No Feature
96	75	6.4
96	60	6.1

Figure 6.8 shows optical microscope images of the patterned features in PMMA with average feature size measurements for each experiment summarized in Table 6.1. SEM images were unavailable due to charging of the insulating PMMA causing difficulty in focusing. The features appear as bright white spots under the optical microscope due to the higher reflectivity of exposed silicon versus PMMA. As focusing voltage is increased, feature size also decreases from 19 μ m at 88 V to 6 μ m at 96 V, indicating a maximum of 17x reduction of the lens diameter. Simultaneously, reducing exposure time to the O₂⁺ beam also resulted in decreasing feature size, though the minimum time required to form patterns was observed to be 60 minutes which was an order of magnitude longer than Si etching experiments with an Ar⁺ beam due to an order of magnitude lower O₂⁺ ion beam flux. Nonetheless, these experiments establish that nanopantography can be extended to materials other than silicon and that it is possible

to pattern carbon-based materials with a O_2^+ ion beam extracted by applying a DC bias in the afterglow of a pulsed O_2 plasma.

6.3. Patterning of Carbon and Graphene with an O₂⁺ Ion Beam

Removal of carbon atoms in graphene by ion beam irradiation is more difficult than in bulk graphite or photoresist due to the 2D structure single-layer structure of graphene. Even when graphene is placed on a bulk substrate such as glass, Si or SiO_2 , the graphene is only weakly bonded to the substrate by van der Waals interactions, disrupting energy transfer to carbon-carbon bonds that normally occur through collision cascade from ion impact to the bulk substrate [160,161]. However, oxygen plasmas generate oxygen radicals and O⁺ ions that chemically modify graphene, allowing graphene to be etched through an ion-assisted mechanism from an oxygen plasma or even through an atomic layer etching mechanism by exposure to oxygen radicals followed by an energetic neutral or ion beam [113,121,122,162]. In this investigation, single layer graphene on silicon samples were patterned via the nanopantography method with exposure to a 100 eV O_2^+ ion beam, 100 eV Ar⁺ ion beam in a background of 10^{-5} Torr Cl₂ gas, and a combination of O_2^+ followed by Ar⁺ ions in a background of Cl₂. The oxygen ion beam was generated via the methods previously described in Section 6.2. After patterning, samples were examined under both optical microscopy and scanning electron microscopy, though patterns were only visible in the optical microscope after generating condensation on the sample surface by exposure to humid air.



Figure 6.9: Patterning of graphene on silicon with varying exposure time to 99.6 eV O_2^+ ion beam with 6.5 eV FWHM. Graphene was grown on copper foil and transferred via the PMMA method.

Figure 6.9 shows patterning of single layer graphene on silicon prepared by CVD growth on copper foil and transferred to the substrate by the PMMA method with acetone treatment. The samples were exposed to the beam for 30, 60, and 90 minutes with 94 V focusing for the 30-minute exposure and 96 V focusing for the longer exposures. The SEM images exhibit four shades on the substrate surface which correspond to four regions: (1) graphene shadowed by the solid portion of the mesh and unexposed to the beam, (2) graphene exposed to light from the plasma and neutrals but shielded from ions due to focusing caused by application of bias, (3) graphene or silicon exposed to the outer edge of focused O_2^+ ions, and (4) graphene or silicon exposed to the point of focused O_2^+ ions. Region 2 always appears darker than Region 1, but Region 3 is darker than Region 2 for 94 V focusing and lighter for 96 V. Similarly, Region 4 appears bright for 94 V and dark for 96 V. The edges of the lens openings are often rough or contaminated with dust particles, causing shadows and rough edges around the circumference. These shadows provide a hint that the surface in Region 2 is being modified by the incidence of neutrals rather than photons, since sharp, sub-micron sized edges with acute angles are reproduced on the substrate surface that are not able to be produced by light due to diffraction.

The two major questions of interest are the identity of the materials on each region and if graphene has been etched. The analysis is further complicated by the fact that the PMMA graphene transfer method tends to leave a thin layer of PMMA residue on the graphene surface without additional chemical cleaning or high temperature (>400

°C) annealing in a reactive gas background [163,164]. The thickness of these residues may vary on each sample, and it was likely that the sample with 30 minute etching time may have had a thinner residue layer, and no conclusion can be drawn despite varying exposure times. Identification of the surface was attempted using Raman spectroscopy, but the graphene signal-to-noise ratio on silicon was too weak to differentiate between the different shaded areas.

To reduce the possible options for material identities, patterning was also conducted on highly oriented pyrolytic graphite (HOPG) substrate (Ted Pella, ZYB, 0.8° mosaic spread), consisting of graphene grains which are highly oriented with respect to each other. HOPG is high purity (>99.99% carbon), so differences in surface shading under SEM will result from defects or surface modification from the beam. Figure 6.10 shows SEM images of a clean HOPG surface before (left) and after 120 min exposure to a 97.2 eV beam with 7.2 eV FWHM at 94 V focusing potential. An 8 µm bright spot is observed in the center of each lens, a nearly 12x reduction of the 100 µm lens diameter and comparable to PMMA patterning results in Table 6.1. Clearly in the absence of contamination, the surface of graphene is modified in a way that increases secondary electron emission, appearing bright under SEM. The outline of the bright central feature is outlined by a darker shade, most likely due to differential charging from the electron beam. The outline of the lens on the HOPG surface due to energetic neutral exposure is also visible, with the region inside the lens appearing darker than the region outside the lens. While SEM images appear to show a smooth surface, AFM and profilometer measurements were unable to characterize height profiles along the sample surface due to large variations in height of HOPG on a macroscopic (>1 μ m) scale and etching still could not be confirmed.



Figure 6.10: HOPG before (left) and after (right) 120 min exposure to O_2^+ ion beam. A zoomed-out view of the sample after exposure is inlaid on the top right.

Since silicon is not expected to etch under exposure to O_2^+ ions alone, additional patterning experiments were conducted using 150 minutes exposure to an Ar⁺ ion beam in a 10⁻⁵ Torr Cl₂ gas background and a combination of 30 minutes exposure to O_2^+ followed by 120 minutes exposure to Ar⁺ in a Cl₂ background. Single-layer graphene on silicon samples were purchased from ACS Materials. Lens diameter was increased by switching to a metal mesh with 170 µm diameter circular openings to increase the ion flux available at the focused spot by a factor of 3. Ion beam conditions were 96.8 eV with 6.8 eV FWHM for Ar⁺ and 95.5 eV with 6.4 eV FWHM for O_2^+ with 94 V focusing used in all experiments. Figure 6.11 shows SEM images of the sample surface after exposure.



Figure 6.11: Patterning of graphene on silicon by exposure to Ar^+ only in a background of Cl_2 (left) and O_2^+ followed by Ar^+ in a background of Cl_2 (right).

The sample surface for both beam exposures shows 3 regions consistent with the patterned HOPG: (1) graphene shadowed by the solid portion of the mesh and unexposed to the beam, (2) a darker shade exposed to energetic neutrals but shielded from ions due to focusing, and (3) a bright spot created by exposure to focused high energy O_2^+ and Ar^+ ions. A darker outline of the bright region due to charging is observed, similar to patterned HOPG samples. The bright focused spots were measured to be an average of 47 μ m in diameter for Ar⁺ only and 31 μ m for O₂⁺ followed by Ar⁺. The spots also appear much higher contrast than in previous patterning experiments due to the larger lens diameter providing 3x the ion flux to the sample surface. Since no hole is observed compared to mesh etching experiments on pure Si, removal of graphene and etching of the silicon surface is not likely. However, in zoomed images of the center of the bright spot region (bottom of Figure 6.11), cracks are visible in both samples. Since cracks do not form in silicon, the bright white spots must result from modified graphene and the cracks may result from preferential removal of graphene at grain boundaries, which has a lower threshold energy for carbon atom sputtering. There does not appear to be any chemical enhancement from O_2^+ ion irradiation, most likely since O_2^+ does not lose enough energy upon impact and dissociation to produce O atoms with low enough energy to be trapped in the potential well of a C-O covalent bond (about 7 eV).

Molecular dynamics studies indicate that the probability of sputtering a carbon atom from a suspended graphene sheet may be as low as 0.01 for 100 eV Ar^+ ions at normal incidence [97,112]. The probability of inducing vacancies by displacing carbon atoms in graphene, differentiated from sputtering a carbon atom from the surface to

vacuum, is more commonly studied and spans a range of 0.01 to 0.2 [97,112,160,165]. Additionally, it has been widely reported that graphene supported on a substrate has a higher energy threshold for displacement than a suspended sheet due to collisions with substrate atoms restricting the displacement of carbon atoms [160]. Maximum graphene sputtering yields were found to approach the sputtering yield of the SiO_2 substrate for 5 keV Ar^+ ions in simulations [160], so it may be reasonable to assume that the maximum sputtering yield of graphene in this study is that of Si, i.e. 0.025 for 120 eV Ar⁺ ions [166]. For the purposes of estimation, minimum sputtering yield will be assumed to be 0.01. The high energy Ar⁺ ion current was measured to be 100 nA over a 1" diameter collector, resulting in a flux of 1.2×10^{11} ions/(cm²-s) at the sample. Assuming a focused spot size of 30 μ m from a 170 μ m lens, the flux is increased to 4 \times 10¹² ions/(cm²-s) and a total dose of 3.6×10^{16} ions/cm² at each focused spot after 2.5 hours of exposure to the Ar⁺ ion beam. The O_2^+ flux is approximately 1/3 of the Ar⁺ flux, and exposure time is 1/5, resulting in an even lower dose of 2.4×10^{15} ions/cm². The area of a graphene unit cell is 0.052 nm² and contains 2 atoms, giving a surface concentration of 3.8×10^{15} cm⁻². Using the assumed sputtering yields, a dose of at least 1.5 to 3.8×10^{17} Ar⁺ ions is required to remove a single layer of graphene, an order of magnitude higher than in this investigation.

Given the resistance of graphene to sputtering of carbon atoms to vacuum by ion bombardment and bright appearance of the focused spots on HOPG and graphene on Si under SEM, it must be concluded that the graphene layer was not removed by either physical sputtering from Ar^+ ions or chemically assisted mechanisms from O_2^+ ions, leaving the underlying silicon unetched. In fact, graphene has been reported to be an excellent shield to prevent the sputtering of underlying material [112,167]. Since the probability for defect formation is higher by an order of magnitude, it is likely that the graphene layer was instead highly damaged by exposure to the ion beam, creating vacancies that reconstruct to disordered and amorphous carbon. In studies of relatively low energy (<200 eV) Ar^+ ion bombardment of graphene on SiO₂, Raman measurements of the surface were indistinguishable from amorphous carbon after bombardment of $10^{15} - 10^{16} ions/cm^2$ [96,99,109,111]. At least 10x higher ion dose at the focused spot are needed to remove the graphene, which can be realized by increasing ion current from the source, exposure time, and optimization of focus. While graphene removal was not demonstrated in this study, the controlled production of defects in graphene was demonstrated and is still of interest for tailoring graphene properties for wide-ranging applications [98,100].
6.4. Summary

An oxygen ion beam generated from the application of synchronous DC bias in the afterglow of a pulsed plasma was characterized via RFEA and time-resolved current measurements, confirming that O_2^+ composed the majority of extracted ions. The O_2^+ ion beam was then used to form patterns on carbon-containing photoresist, HOPG, and graphene on silicon. Graphene was found to be damaged but not removed by exposure to 10^{16} cm⁻² doses of 100 eV O_2^+ and Ar⁺. Comparisons between graphene patterning using an O_2^+ ion beam and Ar⁺ ion beam did not indicate any chemical enhancement of the removal of graphene.

Chapter 7 Conclusions and Recommendations

For decades, researchers have been predicting the imminent arrival of a successor to optical lithography for the continuation of Moore's law below 10 nm. Improvements in phase shift masks, optical proximity correction, immersion lithography, and self-aligned multiple patterning extended the lifetime of 193 nm ArF nearly a decade, but extreme ultraviolet (EUV) lithography has finally arrived. However, the extreme complexity and expense of EUV still presents a substantial barrier to novel niche and research applications, and other technologies such as nanoimprint lithography have made significant progress and are still relevant for low-cost patterning of nanoscale structures and devices. Print-and-repeat nanopantography in particular is useful for patterning arbitrary materials, and the extension of nanopantography to deposition of 3D nanostructures has yet to be explored.

7.1. Conclusions

Nanopantography is a method for massively parallel writing of nano-sized patterns using an ion beam. In this process, a broad area, collimated, nearly-monoenergetic ion beam is directed towards an array of micron-scale electrostatic lenses in direct contact with a substrate. By applying an appropriate DC voltage to the lens array with respect to the substrate, the ion beamlet entering each lens converges to a fine spot that can be 100 times smaller than the diameter of each lens. Previously, lenses fabricated directly on the silicon substrate were used to etch 3 nm diameter holes

in silicon by exposure to a monoenergetic Ar⁺ ion beam and chlorine gas. This work reports on the development of removable and reusable free-standing membrane-based electrostatic lens arrays that are designed to pattern any conducting surface.

7.1.1. Print and Repeat Nanopantography

A process was developed for fabricating reusable membrane-based electrostatic lens arrays for the nanopantography patterning method. Lens arrays were fabricated on silicon wafers using 1 μ m of SU-8 as a dielectric material and copper and gold as the lens electrode. The lens arrays were placed on silicon substrates and biased to +100 V to demonstrate flattening and electrostatic clamping to the substrate surface. Removal of the lens array from the surface was demonstrated by allowing ultraclean deionized water to diffuse under the membrane, lifting the lens off of the surface. The lens arrays were used to etch features on silicon with a 70 eV Ar⁺ ion beam in a background of Cl₂ gas. Experiments were conducted to compare the effect of lens geometry on feature size at a fixed lens focusing voltage and the results were compared to SIMION ion optics simulations, showing reasonable agreement. The removable lens arrays were successfully used to pattern 30 nm features using a 1.5 μ m diameter lens array, a size reduction of 50X. These results demonstrate the feasibility of using reusable and removable membrane-based electrostatic lens arrays for nanopantography.

7.1.2. Lens Simulations

A multiscale model of the system was created using an analytical solution for the macroscopic ~60 cm ion drift region starting from the exit of the ion beam source and the numerical simulator SIMION for the microscopic ion focusing region starting 3 µm away from the lens openings. Simulations were performed to study the relative importance of aberrations resulting from lens geometry, ion energy distribution, and ion angular distribution. Additional simulations were performed to optimize system geometry and lens geometry, resulting in the prioritization of the minimization of ion angular distribution and lens dimensions to ultimately achieve sub-nanometer resolution. Finally, a method was developed to quantify image contrast to select focusing voltages that produce optimum feature sizes when several voltages appear to produce similar sizes.

7.1.3. Graphene Patterning

An oxygen ion beam generated from the application of synchronous DC bias in the afterglow of a pulsed plasma was characterized via retarding field energy analyzer (RFEA) and time-resolved current measurements, confirming that O_2^+ composed the majority of extracted ions. The O_2^+ ion beam was then used to form patterns on poly(methyl methacrylate) photoresist, highly oriented pyrolytic graphite (HOPG), and single layer graphene on silicon. Graphene was found to be damaged but not removed by exposure to 10^{16} cm⁻² doses of 100 eV O_2^+ and Ar⁺. Comparisons between graphene patterning using an O_2^+ ion beam and Ar^+ ion beam did not indicate any chemical enhancement of the removal of graphene.

7.2. Recommendations for Future Work

Nanopantography was previously shown by Tian to be able to produce sub-10 nm resolution with lens diameter and dielectric thickness on the order of 300 nm [29]. In this work, nanopantography was successfully extended to pattern 20 nm features in lens openings on the order of 1 μ m. A logical next-step and important goal would be to demonstrate patterning of sub-10 nm features with print-and-repeat nanopantography, as current low-cost non-EUV lithography methods are not yet capable of producing such small arbitrary features with high throughput. To accomplish this, the lens dimensions need to be reduced radially and possibly axially. However, SU-8 dielectric thickness cannot be reduced freely despite an ideal dielectric strength of 400 V/ μ m, as defects introduced during processing drastically reduce the observed dielectric strength. Dielectric breakdown of a 1 µm SU-8 film was observed even below 70 V in many samples. The lens array fabrication process must be improved to realize a higher yield of usable lens arrays by minimizing contamination and by root cause analysis to identify any failures related to the specific etch and release chemistries. One of the first specific steps that can be taken is to move all sample processing to a cleanroom environment, minimizing contamination that is introduced from transporting the sample between facilities. Simulations should also be conducted to find lens geometries and beam conditions that maximize dielectric thickness while minimizing focusing voltage and

feature size. Yield of usable samples has by far been the most challenging bottleneck in demonstrating further results with print and repeat nanopantography, and continuous yield improvement needs to be given full priority in any actions involving fabrication of new lens arrays.

In the meantime, oxygen beam diagnostics and graphene etching can be further investigated. As a first step, the O_2^+ beam energy should be lowered to verify the hypothesis that the absence of etching is caused by O atoms having too high of an energy to be trapped in a bonded state. Any O atoms that may bond to carbon atoms must be generated from 100 eV O_2^+ collision and neutralization with the graphene surface. While the O_2^+ ion beam should provide sufficient flux for patterning at the sample surface after focusing, increasing the beam flux will speed up processing times, which are currently on the order of hours, and extend the present method of generating an O_2^+ ion beam to other applications in reactive ion beam etching (RIBE). Much of the parameter space for the pulsed oxygen plasma with synchronous dc bias has yet to be explored, and it may be possible to significantly increase flux by adjusting flow rate, pressure, power, pulsing frequency, duty cycle, bias delay. At this point, it is also unknown if the order of magnitude lower O_2^+ current is due to unoptimized operating conditions, lower plasma density, absence of space charge self-neutralization, or some combination of the preceding. Additional diagnostics such as Langmuir probe and moveable Faraday cup could also shed light on the ion and electron dynamics of the plasma and beam, which clearly differ from a beam generated from an Ar⁺ plasma. The foundation gained from understanding O_2^+ ion beam dynamics can then be extended to

generating ion beam sources from other electronegative plasma chemistries such as fluorocarbon, SF₆, and Cl₂, which may have useful applications for RIBE.



Figure 7.1: (a) Sub-10 nm diameter silicon vertically aligned silicon nanowire array (b) Diameter distribution of array. Reproduced from Huang et al. [168]

Deposition is another interesting area that has yet to be thoroughly explored by nanopantography and may be an important focus as other top-down lithography methods can only produce a limited subset of 3D structures. While top-down methods are already capable of manufacturing sub-10 nm vertically aligned nanowire arrays (Figure 7.1), nanopantography should be possible to form 3D shapes with angles, bends, and twists which are unlikely to be produced by any other top-down method. A simple starting point could be the fabrication of vertical nanowire arrays by allowing the ion beam to dwell and deposit on a single spot. Deposition on the top of lens array itself may be a concern, especially if insulating films are deposited, limiting the reusability of lens arrays.

As with optical lithography, different mask shapes should be able to generate different focused patterns on the substrate surface. Lens shapes such as lines or noncircular patterns have yet to be explored for generating patterns with nanopantography. Line patterns with length on the order of millimeters should be explored to test the alignment and straightness of the clamping action in print-and-repeat nanopantography over large distances. Complex shapes such as plus signs can also be used to test sharpness of pattern shrinkage. Alternatively, the lens array could be made from rigid materials, separated from the substrate surface, and translated with respect to the substrate instead of tilting, similar to the approach of Choi et al. [82,83] Translation of either the stage or substrate would be able to connect patterns formed in one lens with adjacent lenses, which is one limitation of the pantography aspect of nanopantography.

In conclusion, there are still numerous research directions that can be taken with nanopantography, and it is the hope of the author of this work that future researchers will take note of the simplicity and wide applicability of its basic principles. Massively parallel focusing of charged particles into nanoscale spots near a surface is a broad topic, and there are applications far beyond etching of small features on silicon for microelectronic circuits.

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