



**Characterization of Reactive Ion Etch
Chemistries Using Direct Write Lithography**

THESIS

Dylan T Martin-Abood, Second Lieutenant, USAF
AFIT-ENG-MS-20-M-041

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DIRECT WRITE LITHOGRAPHY

THESIS

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Degree of Master of Science in Electrical Engineering

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Abstract

Microelectronics and Microelectromechanical Systems (MEMS) are integral to the operational capabilities of the Department of Defense (DoD). The DoD requires a variety of Components off the Shelf (COTS) and number of custom microelectronics to provide important functionality to critical military systems. Today's conflict environment requires flexibility and adaptability to swiftly evolving environments and requirements. Improvements to existing fabrication techniques are required to assure access to rapid prototyping for the development of new technologies and modification of existing ones. Photolithography and Deep Reactive Ion Etching (DRIE) are two techniques commonly used in the generation of deep anisotropic features for the fabrication and modification of microelectronics and MEMS. However, standard photolithography techniques are ineffective for unique substrate geometries. DRIE processes that provide deep anisotropic etch profiles require a chemical passivation step only applicable to silicon (Si) substrates. Although this thesis work restricted its scope to the Reactive Ion Etching (RIE) silicon, the process presented here is intended for application to alternative materials. This work explores the capabilities and limitations of Direct Write Lithography (DWL) and standard RIE to etch deep, anisotropic features on elevated surfaces.

This work confirmed the capability of RIE using DWL to perform deep, highly selective, anisotropic etching on elevated, non-circular substrates. Selectivity studies were performed on three types of Photoresists (PRs) with varying chemical composition and thickness on $\{100\}$ and $\{111\}$ n-type Si wafers. $\text{SF}_6/\text{CHF}_3/\text{O}_2$ was determined to be a far superior reactive gas species over CF_4/O_2 for the deep, selective, anisotropic RIE of Si. RIE treatments with $\text{SF}_6/\text{CHF}_3/\text{O}_2$ yielded average

selectivities of 20.6 for Si:Shipley 1818, 17.1 for Si:Bi-layer PR, and 32.4 for Si:AZ9260. Increasing PR thickness appeared to reduce etch anisotropy. A 46.6 μ anisotropic etch was achieved in {111} n-type Si masked with a 10 μ m mask layer of AZ 9260 PR using standard RIE and SF₆/CHF₃/O₂ as the reactive gas species. Finally, a Heidelberg μ PG101 Micro Pattern Generator was used to perform DWL on a 2000 μ m elevated, non-circular surface.

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Acronyms

AFIT Air Force Institute of Technology. 33, 36

ASIC Application Specific Integrated Circuit. 1, 2

BCC Body-Centered Cubic. 18

COTS Components off the Shelf. iv, 1

CRD Complete Randomized Design. 70

DoD Department of Defense. iv, 1, 2, 7, 1

DOE design of experiment. 51

DRIE Deep Reactive Ion Etching. iv, 6, 1

DWL Direct Write Lithography. iv, xi, 2, 5, 7, 9, 13, 15, 35, 36, 38, 54, 55, 81, 82, 83, 84, 85, 86, 87, 92, 93, 94, 96, 97, 98, 99, 100, 1

EM Electromagnetic. 1, 5, 11, 15, 86

FCC Face-Centered Cubic. 18, 19

FPGA Field Programmable Gate Array. 1

HCP Hexagonal Close Packed. 18

IBE Ion Beam Etching. 23

IC Integrated Circuit. 1

MEMS Microelectromechanical Systems. iv, 1, 2, 6, 7, 9, 12, 15, 20, 96, 99, 1

PAC Photoactive Compound. 3, 10, 86

PE Plasma Etching. 23

PR Photoresist. iv, 3, 4, 5, 7, 9, 10, 11, 12, 13, 14, 15, 16, 23, 26, 32, 33, 35, 36, 37, 38, 39, 43, 44, 47, 50, 51, 52, 53, 54, 55, 57, 75, 76, 81, 86, 87, 88, 89, 91, 92, 94, 97, 98, 100

RIE Reactive Ion Etching. iv, xi, 2, 6, 7, 9, 11, 22, 23, 27, 31, 32, 33, 35, 36, 37, 38, 39, 40, 47, 48, 50, 51, 54, 56, 57, 64, 80, 81, 85, 86, 90, 91, 94, 96, 98, 99, 100, 1

Si silicon. iv, 2, 5, 6, 7, 16, 17, 18, 19, 20, 21, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 39, 50, 54, 56, 75, 76, 87, 91, 94, 96, 97, 100, 1

SoC System on Chip. 1, 2

UV Ultraviolet. 15, 16, 50

CHARACTERIZATION OF REACTIVE ION ETCH CHEMISTRIES USING DIRECT WRITE LITHOGRAPHY

I. Introduction

1.1 Problem Background

Microelectronics and Microelectromechanical Systems (MEMS) are fundamental to the technologies and capabilities that enable Department of Defense (DoD) operations. The DoD requires a variety of Components off the Shelf (COTS) and number of custom microelectronics. Integrated Circuits (ICs), Application Specific Integrated Circuits (ASICs), System on Chips (SoCs), and Field Programmable Gate Arrays (FPGAs) operate critical systems including radar, optics, communications equipment, biomedical devices, GPS. MEMS are used in a variety of military applications including sensing, optics, and switching. The current and future DoD operational environment require advanced development in both the capability of these devices and the processes used to create them. Additionally, great emphasis must be placed on adaptability, flexibility, and rapid prototyping to develop and field new technologies or modify existing ones.

A number of techniques and processes are used to fabricate microelectronics and MEMS devices. Two commonly employed processes are Photolithography and etching. Photolithography provides the design blueprint and etching produces the final design in the substrate material. In photolithography, Electromagnetic (EM) radiation (light) transfers the pattern onto a photosensitive substance applied to the surface of the material. Etching provides the mechanism to transfer the design onto

the material. The etching mechanism can be chemical, physical, or a combination of both.

Due to its favorable electronic and mechanical properties, silicon (Si) has become the material of choice for microelectronics and MEMS. However, a variety of materials are utilized dependent on the desired application, function, and properties of the device. The effectiveness of etching mechanisms rely on the target material's atomic structure. Sufficient energy, either kinetic or chemical, must be supplied must to break the atomic bonds of the material. In a chemically driven etching process, reactive species must react with the substrate material and the reaction products must then be removed from the surface to allow etching to continue. Reactive Ion Etching (RIE) is a physically assisted chemical dry etching process that can be applied to a variety of materials.

Photolithography is a technique best employed on homogeneous planar surfaces. Non-planar, elevated, and unique geometries create obstacles rendering traditional photolithography techniques ineffective and are described further in Section 2.2.3. Direct Write Lithography (DWL) has the capability to work around these difficulties. There has been growing interest in using DWL methods to rapidly produce new designs and modify existing devices. DWL can be used to develop new structures, contacts, and components to pre-existing microelectronics and MEMS.

Military applications often require unique custom SoC and ASIC. These devices have high production costs, require long development and manufacturing times, and leave no opportunity for post-production alterations [12]. To meet DoD demands non-trivial photolithography and etching techniques are required to reduce costs and production times, improve performance, and expand functionality. This work seeks to determine the viability of DWL and RIE to address these challenges for certain applications and expand upon current fabrication capabilities in the fields of micro-

electronics and MEMS.

1.1.1 Direct Write Lithography (DWL)

Photolithography is well studied and used throughout the fields microelectronics, microfluidics, and microelectromechanical (MEMS) systems. Optical lithography is the most commonly used photolithography technique. In optical lithography a photo-sensitive layer known as Photoresist (PR), a compound which contains a Photoactive Compound (PAC), is spread onto the substrate material. Different PRs, each containing a different PAC can be applied to the surface of a material dependent on the light exposure source. PACs react to specific wavelengths of light. Once the PR is exposed in the desired pattern a developing chemical removes unwanted PR from the material surface. The remaining PR serves as a protective mask during etching, when the design is permanently transferred to the target material's surface. Figure 1 depicts the basic steps of etching with photolithography.

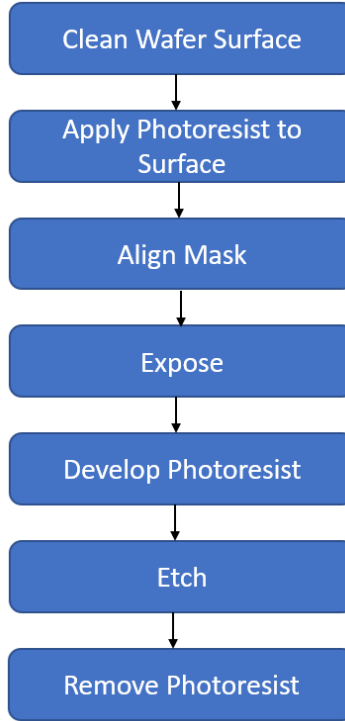


Figure 1: Basic steps in the photolithography and etching process.

In the photolithography process shown in Figure 1, a pre-fabricated mask is aligned between the substrate surface and flood exposure source. The mask ensures only the desired exposure pattern is transferred to the PR. Photomasks are typically fused silica covered with an opaque layer of chromium. Fused silica has a high degree of optical transparency while chromium blocks incident light. The chromium pattern on the fused silica determines the exposure pattern that will pass through the mask into the PR.

It is important to clarify early in this work that the word "mask" is used to define two aspects of photolithography. In the first case, a photomask, also known as simply a "mask," is used to filter a flood exposure by allowing only the desired pattern of light to pass through. In the second case, the PR pattern that remains on the surface after development serves as a protective "mask" for the substrate. This work seeks to

remove the first photomask from the process entirely while maximizing the durability and longevity of the protective PR mask.

Although transparent, the fused silica photomask will still reflect, absorb, and phase-shift incident radiation to some degree [13]. Photomasks can be used in contact, proximity, and projection mode. Each method has its own advantages and disadvantages impacting feature resolution and defect generation. Contact lithography provides high feature resolution as long as the PR has uniform contact with the mask. This eliminates the gap between the wafer and mask and minimizes diffraction effects [13]. However, any non-uniformity in the PR will generate undesired light diffraction. Direct contact between the photomask and wafer can also introduce defects. Proximity lithography eliminates the risk of generating defects, but compromises feature resolution. Projection lithography can provide the highest resolution of the three modes without generating defects but still requires that a be generated to project the desired pattern.

Creating photomasks can be expensive. Typical Si technology can require tens of masks or more. Designing and making each photomask can be expensive and slow leaving little opportunity for future scaling of dimensions. Photolithography accounts for nearly one-third of overall fabrication cost, a set of photomasks for producing a chip can exceed \$2 million, and yet in most cases only a few wafers will be produced[13]. The difficulties in designing and repairing a mask can delay production time and increase costs.

DWL offers a path around these difficulties by completely removing the photomask from the process [14]. In DWL the exposure pattern in the PR is created using a directed beam of EM radiation. DWL is far too slow for any batch processing, but well suited to provide rapid lithography for unique, custom designs. This work explores the direct-write capabilities of the Heidelberg μ PG101 Micro Pattern Generator which

uses a 1 μm , 18 W, 375 nm beam exposure source to generate patterns.

1.1.2 Reactive Ion Etching (RIE)

RIE is a kinetically enhanced dry chemical etching process used in the fabrication of microelectronics and MEMS. The mechanism of any etching process can be physical, using kinetic energy to remove atoms, chemical, using reactions between the material surface and volatile reaction species, or a combination of the two. The dominating mechanism and substrate atomic structure impact etch rate, selectivity, and anisotropy of etch. These important etch characteristics are expanded upon further in Section 2.5.

RIE has the ability to create a more anisotropic etch than purely chemical etching processes and higher selectivity than purely physical processes such as ion milling [13]. RIE can be used to sputter metals and etch silicon-based, dielectric, compound, diamond-like, and photo-resist materials. RIE is best described as "ion-assisted etching" and uses a combination of both physical and chemical etching. RIE can achieve relatively deep, high resolution trenches to be used in a variety of applications.

Bosch and cryo-processes are the most commonly used Deep Reactive Ion Etching (DRIE) techniques [4] [15] [16] [17]. Bosch and cryo-processes utilize fluorine based chemistry for their high etch rates and selectivities. However, fluorine chemistries are intrinsically isotropic. The most critical factor in achieving deep anisotropic etching through these processes is sidewall passivation, the formation of a protective sidewall layer to prevent isotropic behavior. Sidewall passivation is further described in Section 2.5.4.

Although this work only explores the RIE of crystalline Si, a material capable of achieving sidewall passivation through standard DRIE processes, this work is intended to provide process proof of concept to be applied to additional materials as discussed

in Section 5.5. Therefore, DRIE was not performed. Instead, only standard RIE processes for achieving deep etches were examined.

1.2 Research Objectives

This work focuses on determining the viability of using DWL to overcome challenges post by traditional photolithography for the RIE of Si and additional materials microelectronics and MEMS development and modification. The ability of DWL to produce high resolution features on elevated non-circular substrate surfaces is explored. Three PRs acting as a masking layer for crystalline Si undergoing RIE with two reactive gasses and various RIE chamber factor levels are studied to determine the ideal conditions for achieving maximum selectivity and their anisotropic behavior is studied. This work ultimately determined the capabilities, limitations, and direction of future research for a process utilizing DWL and standard RIE for microelectronics and MEMS fabrication and modification.

1.3 Research Progression

Chapter II provides the accumulation of background information most critical to this work and achieving the research objectives. Topics include etching considerations for crystalline and silicon substrates, DWL and its advantage over traditional photolithography in certain applications, PR characteristics and properties, and the operating mechanisms and characteristics of RIE. Chapter III lays out the methodology and procedures performed to realize the overall research goals. Chapter IV analyzes the gathered data and experimental results. Finally, Chapter V summarizes the results, the success in meeting research objectives, and provides opportunities for future work.

1.4 Defining the Problem

This chapter provided a brief overview of DoD microelectronics and MEMS priorities. Also presented was the origin of this thesis and the research problem that drove the exploration for the appropriate theory and background required to develop the methodology, obtain data, analyze results for conclusive observations and realize direction for future research regarding the viability and capability of employing RIE with DWL to perform deep, highly selective, anisotropic etching on elevated surfaces.

II. Background and Literature Review

2.1 Applicable Background and Theory

This chapter introduces key concepts and theory required to develop the methodology to realize the overall research objectives. Topics include etching considerations for crystalline and silicon substrates, Direct Write Lithography (DWL) and its advantage over traditional photolithography in certain applications, Photoresist (PR) characteristics and properties, and the process, mechanisms, and characteristics of Reactive Ion Etching (RIE).

2.2 Photoresist

This section provides an overview of PRs, their properties, application via spin-coating, and the difficulties which arise when applying PR to non-circular and elevated substrates.

2.2.1 PR Characteristics and Properties

PRs are light-sensitive polymeric resins which serve as masking materials in a photolithographic process. They can be used as structures or to transfer patterns to be etched on a substrate in the development of Microelectromechanical Systems (MEMS).

In an etching process, PR acts as a protective barrier for the areas of the wafer surface which are not to be etched. Polarity is one basic characteristic of PR. The UV exposed regions of a positive PR will dissolve away more quickly when a developing chemical is applied, while the UV exposed regions in a negative PR will remain behind. When exposed to light, negative PR undergoes cross-polymerization to strengthen the bonds. However, this can also result in swelling, therefore reducing resolution.

Negative PR is generally not well suited for feature sizes under $2\text{ }\mu\text{m}$. Positive PR typically has the best resolution and are therefore preferred in most cases [13].

PR typically has three main components: a resin or base material, a Photoactive Compound (PAC), and a solvent that impacts the mechanical properties such as viscosity, keeping the PR in a liquid state to be uniformly spun onto the wafer surface. In positive PR, the PAC slows the rate at which the PR dissolves by acting as an inhibitor before exposure. Exposure to UV radiation activates a chemical process turning the inhibitor to a sensitizer and increases the dissolution rate [13].

Two metrics most commonly used to evaluate a PR are sensitivity and resolution. "Sensitivity" is defined by the amount of light energy required to create the chemical change aforementioned. Light energy is determined by the wavelength and time of exposure [13]. The higher the sensitivity, the less light energy required to induce chemical change. "Resolution" refers to the smallest feature that can be reproduced by the PR. This metric is also greatly impacted by the exposure tool and PR application process [13].

2.2.2 PR Application via Spin Coating

The spin coating process involves four basic stages resulting in the application of a uniform layer of PR on the substrate. Figure 2 depicts the process used in this experiment.

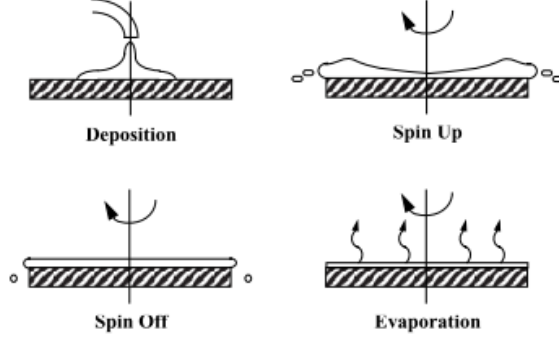


Figure 2: Spin coating stages [1]

Evaporation begins as soon as the PR is dispensed and continues throughout the process while deposition, spin up, and spin off occur in sequential steps. During deposition liquid PR is deposited onto a stationary or slowly spinning substrate. Excess PR is deposited to ensure that the PR does not dry or crack before reaching the wafer edge, creating a uniform layer across the entire substrate. Spin coating is very inefficient. Approximately 95-98% of the deposited PR is flung off and disposed of during spin on [2]. During, or immediately after deposition, the wafer is spun at a "spread speed," typically ranging from 300-500 RPM, allowing the PR to be spread across the surface of the substrate.

In the spin up stage, the substrate is accelerated to a much higher "spin speed," ranging from 1500 to 8000 RPM. Rotational forces form a wave front pushing PR to the substrate edge through centrifugal force. Next comes the spin off stage when excess PR is flung off the substrate surface and enough solvent is removed to raise the viscosity level and cease the flow of PR. Final thickness can be altered by changing the spin speed or PR viscosity. PR thickness is found to vary with spin speed as in 1 [18].

$$T_R \propto 1/(\sqrt{\omega}) \quad (1)$$

Increasing viscosity and reducing spin spin will result in thicker layers of PR. After the spin on process is completed, a softbake is performed to evaporate the remaining solvent and establish the exposure characteristics of the PR [19]. The temperature and time of the softbake affects the sensitivity, contrast, and characteristics of the photochemistry in the PR, all critical aspects to the resolution that can be attained in the remaining lithography process steps. Proper softbake parameters are determined empirically through trial and error. Once the softbake is performed, the PR is exposed to Electromagnetic (EM) radiation which reacts with the photoactive compound in the desired feature pattern. Next, the exposed pattern is removed by a developer solution. The developer solution can be applied through immersion, puddle development, or by a spray system [20] [21]. If desired, a high temperature hardbake can be performed to cross-link the PR to protect it against future energetic process such as RIE. However, a hardbake can cause resist reflow and effect the contrast of patterned features [13]. After these steps are performed the wafer is ready to be etched.

2.2.3 Problems Spin Coating Non-Circular Surfaces

Most microelectronic and MEMS devices in their final form do not have a planar surface or circular geometry. There are three problems that arise when spin coating rectangular substrates: edge beading, geometrical and Bernoulli effects. Edge beads result in a non-uniform PR thickness and impact the resolution and sensitivity of features. Edge beads occur regardless of substrate geometry but become especially problematic when spin coating small and rectangular substrates. The viscosity and surface tension of the PR result in a constant angle at the solid-liquid-gas interface as shown in Figure 3 [2].

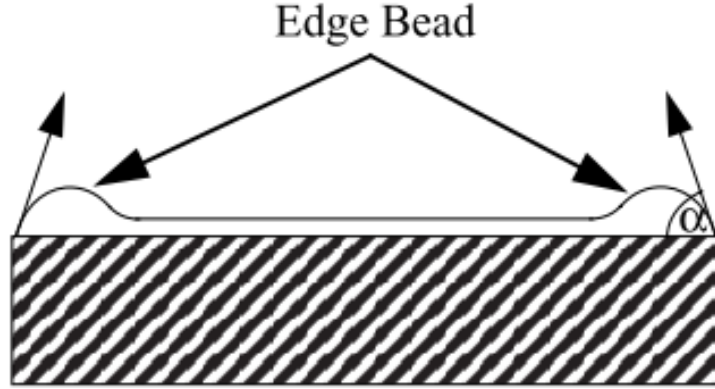


Figure 3: Edge beading [2].

Fluid properties and spin parameters contribute to edge beading. Increased air friction at the periphery of the substrate dries the edge beads first, forcing fluid to flow over the edge beads and dry, increasing the effect. Solvent rich spray can be applied while a circular substrate is spinning to weaken the bead and cause it to fall but this is not possible with rectangular substrates due to lack of radial uniformity [2]. Bevelling the edges of the substrate neutralizes the contact angle shown in Figure 3, flattening the edge bead. However, the excess fluid on the bevelled edge can fall off during later processing steps and cause damage or contamination. Edge beading can cause significant reduction in feature resolution when performing photolithography using a mask in either contact or proximity mode. Assuming that no etching needs to occur on the edges of the substrate, DWL offers the potential to still realize high resolution features when edge beading is a major concern.

Geometrical effects appear on the PR at the corners of rectangular substrates. Figure 4 depicts the geometric effect of spin coating PR onto rectangular substrates.



Figure 4: Geometric effects of spin coating photoresist onto rectangular substrates [3].

At the corners increased air flow cause friction which increases evaporation [3]. PR at the corners dries more rapidly than at the edges, impeding fluid flow and resulting in material buildup.

Bernoulli effects are commonly found in aeronautics and fluid dynamics and the result of an airfoil created between the leading edge of a substrate and the contact angle of the edge bead [3]. Figure 5 depicts this effect.

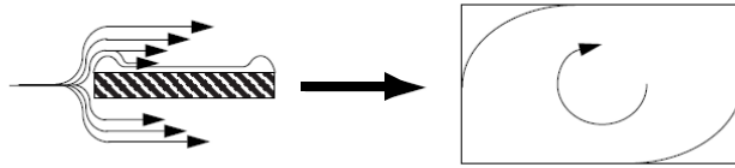


Figure 5: Bernoulli effects when spin coating photoresist onto rectangular substrates [3].

The edge bead creates an airfoil. Air flowing over the top of the substrate has a longer path and thus accelerates while the air flowing below the substrate decelerates generating lift. This significantly enhances the evaporation rate on the surface causing

anywhere from 200 to 500 percent buildup of PR on the corners [3].

The buildup of PR on the edges and at the the corners of rectangular substrates creates serious problems for photolithography methods using hard contact masks for exposure. Non-planar contact and the gap formed between the center of the substrate and the mask significantly reduces resolution due to diffraction, phase-shift, and light scattering effects.

This work utilized DWL to work around the problems created by these effects for mask alignment and exposure. However, the DWL solution is only applicable under the assumption that features do not need to be generated on the edges or corners of a rectangular substrate. If features need to be generated at these locations, alterations to the spin-coating process must be made to reduce these effects and are discussed further in Section 5.5.

2.3 Direct Write Lithography

Photolithography is the process of using photons to transfer a pattern onto a material and is used to create a variety of microelectronic, microfluidic, and microelectromechanical devices and systems. Photosensitive material known as PR is exposed to EM radiation to create a pattern of surface features. Typically photolithography utilizes a mask to transfer the desired pattern via operation in contact, proximity, or projection mode.

Maskless photolithography, also referred to "direct write lithography (DWL)" simply removes the mask from the process by directing a fine beam of Ultraviolet (UV) radiation, instead of a filtered flood exposure, to achieve the desired pattern. The DWL process can serve a number of applications including semiconductor devices, magnetic information stroage, microphotonics, MEMS, microfluidics, and nanotechnology [22].

The exposure of PR by UV radiation is directed from a source system. This system consists of the light source and any optics used to collect, collimate, filter, and focus the light source. The wavelength of the UV radiation generated by the exposure source is critical to the resolution of features that can be exposed. Typically, the shorter the wavelength, the better the resolution. The resolution of an optical lithography system is typically expressed by the relationship shown in (2) [14].

$$W_{min} = k_1(\lambda/NA) \quad (2)$$

Where W_{min} is the width of the smallest feature, or resolution. λ is the wavelength of light, and NA is the numerical aperture of the projection optic. k_1 is a proportionality factor determined empirically which accounts for effects from the resist process [23]. Resolution is not a fixed number for any given optic and alignment system. Resolution is highly dependent on both the optic system and the ability of the PR to react desirably during exposure and reproduce the pattern[13].

Ultraclean conditions are required during photolithography. With device sizes ranging from the nanometers to microns, any dust particles or contamination introduced during the process can produce malfunctions in devices. Therefore, photolithography is performed in clean rooms which are categorized based on the maximum number of particles per cubic meter of air. For example, the Air Force Institute of Technology maintains a Class 100 Clean Room which correlates to an environment containing no more than one hundred $0.5 \mu\text{m}$ particles and less than one $5 \mu\text{m}$ particle per cubic foot.

First, the wafer's surface is cleaned. Then, a layer of PR is applied to the wafer. Next, the PR is exposed to UV laser radiation in a predetermined pattern and immersed in a chemical developer solution. The developing chemical selectively removes the desired patterned PR exposing that same pattern on the substrate surface. The

PR that remains behind forms a protective barrier for the areas of the wafer which are not to be treated or etched. Finally, the silicon (Si) wafer is etched and the residual PR is removed. The end result is a Si wafer with etched features corresponding to the original pattern. Figure 6 depicts the process used in this experiment.

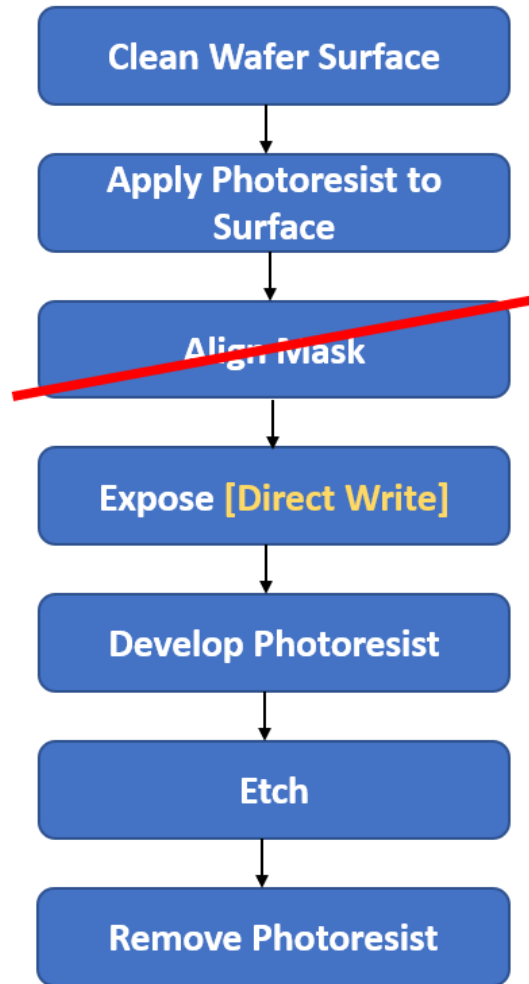


Figure 6: Typical maskless photolithography process.

2.4 Material Crystal Structure and Orientation

Crystal structure has important implications for etching rate and anisotropy. This section outlines the basic nomenclature of the general crystal structure and describes

the crystal structure of Si.

2.4.1 Miller Indices and Crystal Unit Cell

Directions in crystals are determined using a Cartesian coordinate system $[x,y,z]$. Miller indices offer convenient way to describe atomic planes and directions within a crystal lattice. Figure 8 shows the different atomic planes of a cubic unit cell.

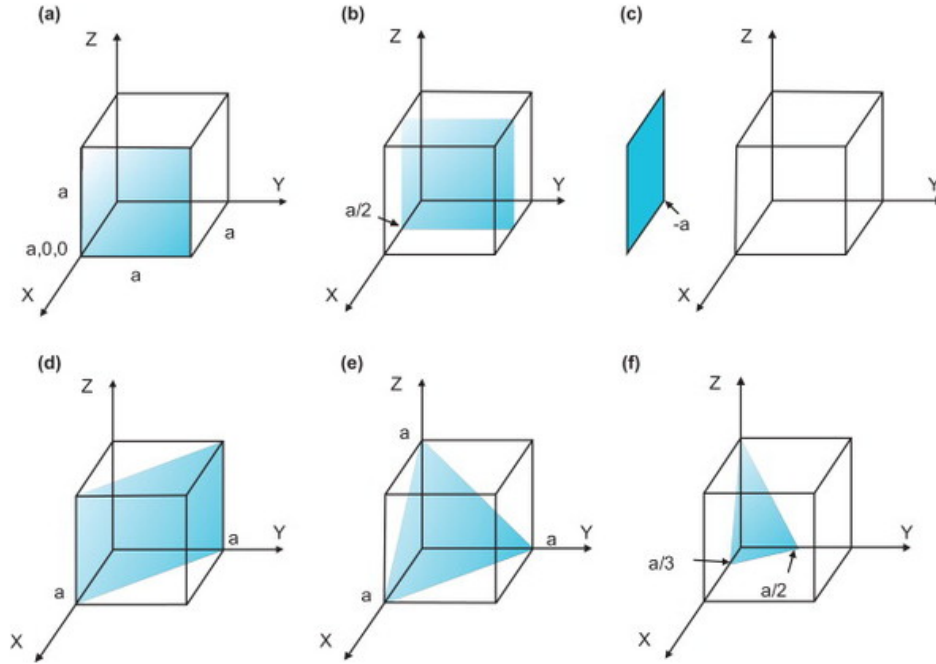


Figure 7: Miller Indices [4]

Crystals are characterized by the three dimensional unit cell, their most basic structural element. The crystal is simply an array of these unit cells repeated regularly over three dimensions. The most common basic crystal unit structures are Hexagonal Close Packed (HCP), Body-Centered Cubic (BCC), and Face-Centered Cubic (FCC). Si crystallizes in a variant of the FCC structure.

The overall FCC structure includes three layers (A,B,C) of hexagonal planes stacked in a way where each layer occupies different vertical positions. Like the

HCP it has an atomic packing factor of 0.74, the densest possible packing factor of any unit cell.

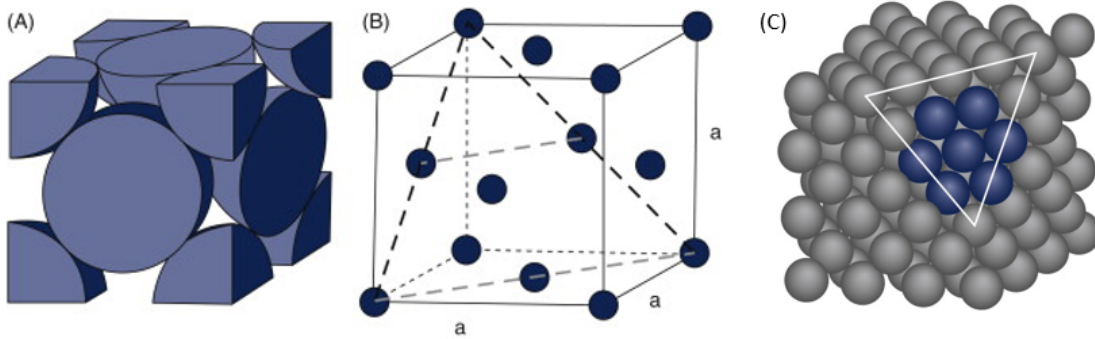


Figure 8: Face centered cubic (FCC) unit cell structure. (A) Representation of atoms to imitate real-size. (B) Representation of atoms as points in the unit cell. Dotted lines show half a hexagon in the dense plane of atoms (C) Truncated FCC crystal structure to show hexagonal close-packed planes [5].

The FCC atom contains four total atoms. Each face centered atom is shared between 2 unit cells ($6 \times 1/2 = 3$), each corner atom is shared between 8 unit cells ($8 \times 1/8 = 1$), resulting in a total of 4 atoms in a FCC unit cell.

2.4.2 Silicon Crystal Structure

Si is a group IV semiconductor element with a diamond crystal structure. Si's diamond structure can be represented as two interlocking FCC lattices that are offset by $(a/4, a/4, a/4)$. Each atom has four valence electrons. To fill the remaining four vacancies in the valence band each Si atom forms covalent bonds with its four nearest neighbors. Figure 9 shows the diamond structure of the Si unit cell.

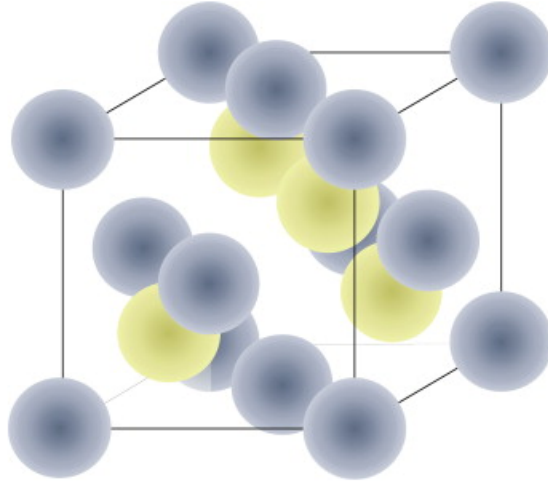


Figure 9: The silicon diamond structure lattice unit cell. Gray silicon atoms in the lattice are in the fcc position, and light color atoms are shifted from fcc positions toward the $[111]$ direction by $1/4$ unit cell length.[4]

Si's atomic properties and crystal structure provide it with favorable electrical and mechanical characteristics, making it the most common material used in micro-electronics and MEMS. Table 1 lists some material properties of Si.

Table 1: Basic material properties of silicon [11]

Property	Value
Atomic Number	14
Atomic Mass	28 (92.23%)
Crystal Structure	Diamond
Lattice Constant	0.357 nm
Si Atoms	5×10^{22} atoms*cm ⁻³
Melting Point	1687 K
Specific Density	2.329 g*cm ⁻³ at 298 K
Thermal Conductivity	149 W*m ⁻¹
Coefficient of Thermal Expansion	2.56×10^{-6} m ⁻¹ K ⁻¹ (at 298 K)
Young's Modulus	150 GPa

Si wafers are manufactured using a process called Czochralski (CZ) growth named after Jan Czochralski who used initially discovered the process as early as 1918 and used it to draw thin metal filaments [13]. The CZ growth process used today throughout the microelectronics field was first developed by Teal [24]. For extremely high purity Si, float zone refining can be used. These processes produce a boule of Si crystal grown in a specific crystal orientation. Flats are then ground to indicate the crystal orientation of the wafer surface. The primary flat, the largest is oriented perpendicular to the $\langle 110 \rangle$ direction. Secondary flats indicate the crystallographic orientation of the wafer surface. Figure 10 depicts the standard flat orientations of Si Wafers.

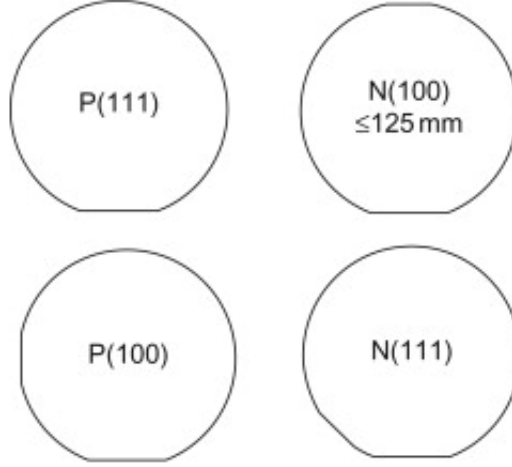


Figure 10: Silicon wafer surface crystal orientation and their associated flats [4].

2.5 Reactive Ion Etching (RIE)

RIE is a well-studied and utilized etching process with a number of applications and variations. This section discusses the RIE background theory and information most applicable to this thesis work.

2.5.1 Etch Properties and Characteristics

A characteristic parameter of the etching process is etch rate expressed as:

$$v = d/t \quad (3)$$

Where d is the distance etched and t is the etching time. Etch rate is affected by the transport and adsorption of reactants to the crystal surface, the chemical surface reaction, and the desorption and removal of reaction products.

There are two primary etching processes; transport controlled and reaction controlled. In a transport controlled process the transport of reactants drives the etch and result in a more isotropic etch. Reaction controlled processes are affected by the

adsorption, reaction, and desorption and result in a more anisotropic etch [9]. Etch processes are typically a combination of the two but characterized by the controlling mechanism which dominates the process.

2.5.2 RIE Process

RIE is an important enabler in microtechnology as it has the ability to etch micro and nano-scale geometries with directional control. Dry etching can be purely chemical as in Plasma Etching (PE), purely physical as in Ion Beam Etching (IBE), or a combination of both as in RIE. Compared with pure plasma etching, RIE is far less directionally dependent on crystal orientation, has the ability to transfer lithography patterns onto substrate surfaces with high resolution and aspect ratios [6]. IBE involves no chemical reactions with etch species and is analogous to sputtering. IBE provides directionality regardless of the material but has extremely low selectivity to PR and any taper in the masking layer will be transferred to the pattern[13]. Figure 11 shows the difference in etch profiles between PE, RIE, and IBE.

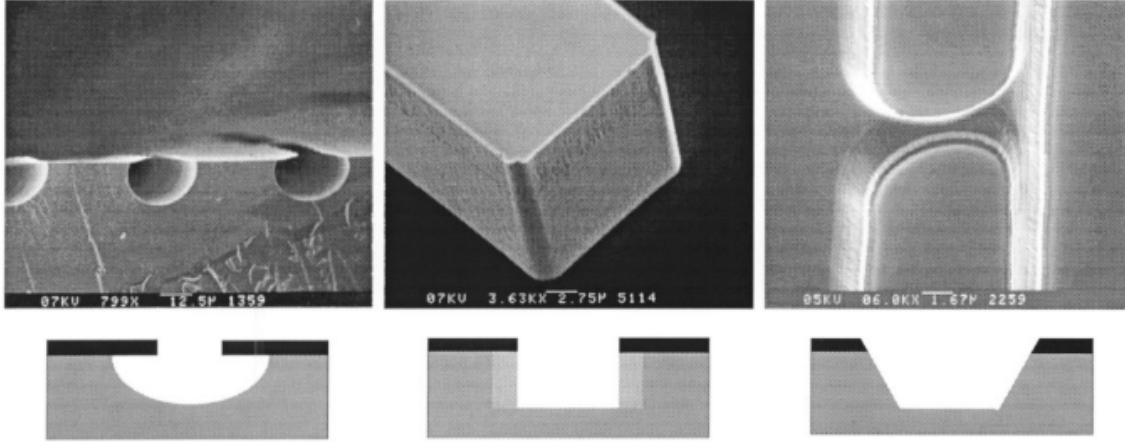


Figure 11: Typical etch profiles of dry plasma etching. Left: Purely chemical isotropic plasma etch (PE). Middle: Anisotropic Reactive Ion Etch. Right: Purely physical Ion Beam Etch (IBE) showing tapering [6]

Reactive Ion Etching (RIE) has the best capability among these three plasma etching processes to provide highly selective anisotropic etching [13] [25]. As ions only account for a very small percentage of species present in the chamber (0.001%), this process is best described as ion-assisted etching [4]. The process uses ion bombardment to assist the chemically reactive plasma used to etch the target. Figure 12 depicts the basic RIE system and process.

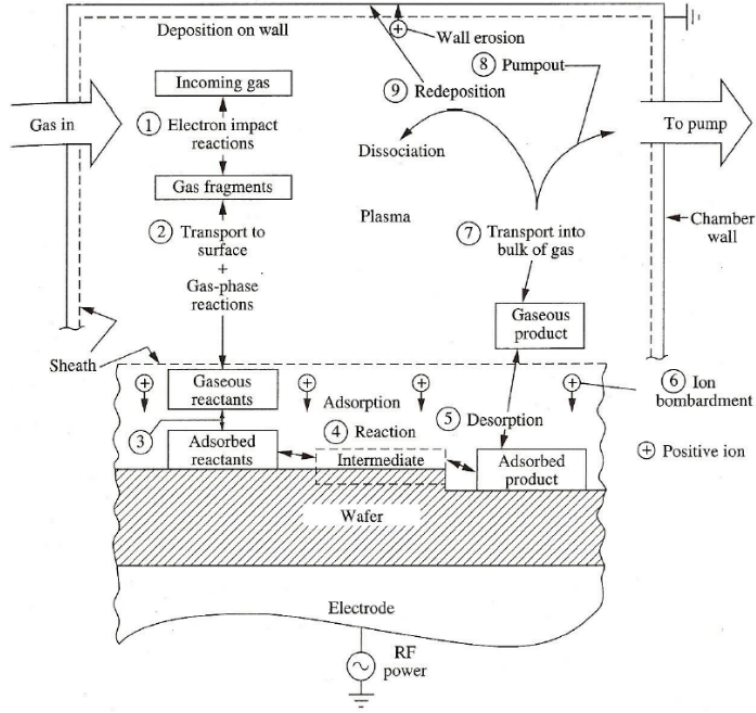


Figure 12: Overview of RIE chamber and process [7].

Each step in Figure 12 is described by the following processes [8].

- Active species generation: A suitable feed gas consisting of radicals, positive and negative ions, electrons, and neutrals is generated by electron impact dissociation/ionization.
- Formation of dc bias for ion acceleration: the substrate material rests on a high frequency driven capacitively coupled electrode. The electrode acquires a negative charge (self-bias voltage) since the mobility of electrons is much greater than that of the ions. This allows the material placed on the electrode to be exposed to positive ion bombardment.
- Transport of the plasma-generated reactive species to substrate surface: this step is driven by diffusion which can limit etch rate in narrow, deep trenches.

- Adsorption of reactive radicals to substrate surface: Concurrent ion bombardment enhances this step by removing the passivated surface layer and producing "active sites" on the substrate surface for radicals to react with.
- Reaction between the adsorbed species and material to be etched: Produces volatile species or their precursors. The reaction rate in RIE is much larger than non-plasma environments due to plasma-induced formation of reactive radicals and ion bombardment.
- Desorption of volatile reaction product into gas phase: Highly critical to the overall etching reaction. Requires that the reaction product has a high vapor pressure at the substrate temperature (typically below 100°C in RIE). Removal is greatly enhanced by ion bombardment.
- Removal of volatile reaction product: Requires the desorbed species to diffuse away from the substrate surface and re-enter the plasma bulk so it can be pumped out. Failure to remove reactive products can lead to dissociation and redeposition.

The wafer patterned with PR is placed inside the chamber. A combination of gasses, with flow rates measured in standard cubic centimeters per unit (SCCM), are pumped into the chamber. Each gas's flow rate can be manipulated to provide the desired etch parameters. Chlorine, fluorine, iodine, and bromine plasmas can be used as etchants. Additive gasses such as oxygen, hydrogen, argon, helium, and nitrogen modify the plasma's thermal characteristics, chemistry, and physics[4]. The plasma combination of etchant and additive chemically interact with the Si atoms to remove them layer by layer. The wafer areas covered by PR are protected from the etching species, while the pattern of wafer exposed is etched. However, additives such as oxygen Etch rate is dramatically increased by ion bombardment which increases

the plasma's surface penetration and supplies energy, increasing the mobility and reactivity of surface species[13]. Surfaces perpendicular to ion bombardment etch much faster than the vertical sidewalls thereby creating a highly anisotropic etch.

The difficulty of independently controlling the temperature and fluxes of reactive species has caused inconsistencies in the reports concerning the F^- based RIE of Si [6]. However, process variables such as radio frequency (RF) power, pressure, etch gas flow rates, and temperature can be used to optimize etch rate, selectivity, and anisotropy of the etch.

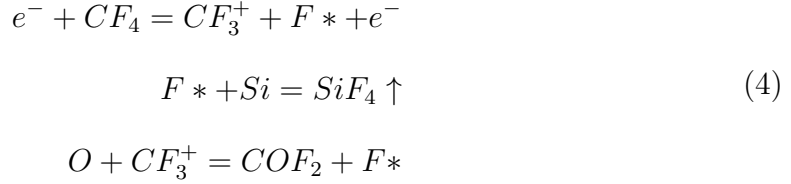
2.5.3 RIE Chemistry and Ion Bombardment

Etching of Si can be done using F^- , Cl^- , and Br^- based chemistries. This work focuses the etching characteristics of CF_4/O_2 and $SF_6/CHF_3/O_2$ plasmas.

Fluorocarbon gases are used frequently for the RIE of Si. Ionized fluorine atoms react with Si removing them from the surface and producing gaseous biproducts such as SiF_4 . CF_4 is a widely used etchant of Si. Mogab studied the etching of Si in a CF_4 with negligible ion bombardment, finding there was a one-to-one relation of Si etch rate and atomic fluorine emission as RF power varied, which indicated that the gas phase density of F atoms controls the rate of Si etching [26]. It has been found that the addition of O_2 with CF_4 results in a much higher etch rate [27]. Mogab *et al.* were among the first to use a parallel-plate reactor to etch Si in CF_4/O_2 plasmas. They reported an etching rate of 3500Å/min at 5% addition of O_2 . With the addition of O_2 the etching rate increased nearly linearly [28]. Oxygen reacts with the etchant gasses and biproducts, keeping the fluorine concentration high and preventing recombination [29].

Zhang *et al.* explored the selectivity and etch rates of Si and SiO_2 and found that CHF_3 provides better selectivity over CF_4 but CF_4 provides a faster etch rate [30].

The reaction between Si and F^* is spontaneous and etching with CF_4 and O_2 results in the following reaction [29].



Chaudhary *et al.* studied the etch rates of Si and SiO_2 using RIE and found that etch rates increase with rising power up to 70% and pressure up to a value of 0.1mbar, after which etch rates drop. The increase in power leads to greater ionization and more free radicals to drive the etching mechanism. However, increasing pressure to a level too great decreases the mean free path of radicals causing ions to collide with each other rather than the surface [29].

Coburn and Winters made an important discovery which determined that the Si erosion rate for a surface simultaneously exposed to both a chemical etchant and Ar ion beam is much greater than the sum of their etch rates when exposed separately [31].

Some models describing the mechanisms for enhanced etching driven by ion-induced reactions are:

- Chemically enhanced physical sputtering [32]. Here the bond of the modified surface layer (eg; SiF_4) are less tightly bound than Si resulting in a greater sputtering yield.
- Damage model [33]. By damaging the crystal lattice structure through ion bombardment the reaction rate is increased at those locations.
- Chemical sputtering model [34]. Ion bombardment supplies physical energy

through collisions which increase the mobility of molecules allowing for easier formation of volatile products and desorption into the bulk plasma gas.

The effect and function of each gas in a $\text{SF}_6/\text{O}_2/\text{CHF}_3$ plasma on etch characteristics are well understood allowing etch profile to be controlled by adjusting the flow rate of these gases [6]. SF_6 provides the F radicals for the chemical etching of the Si and forms volatile SiF_4 , oxygen creates the O radicals to passivate the Si surface with $\text{Si}_x\text{O}_y\text{F}_z$, and both CHF_3 and SF_6 responsible for the removal of the $\text{Si}_x\text{O}_y\text{F}_z$ layer at the trench bottom forming the volatile CO_xF_y or SO_xF_y [6]. Figure 13 depicts the etching mechanisms of a $\text{SF}_6/\text{O}_2/\text{CHF}_3$ plasma.

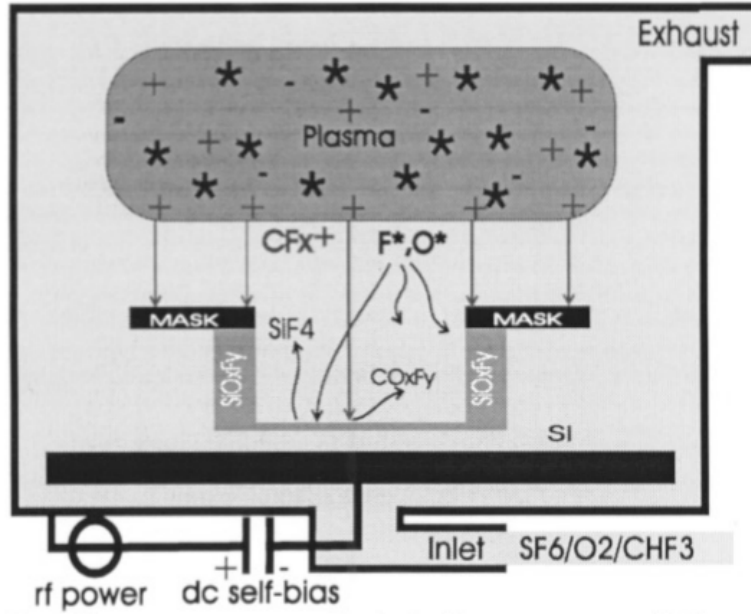


Figure 13: RIE process with $\text{SF}_6/\text{O}_2/\text{CHF}_3$ plasma [6].

The addition of CHF_3 gas does not play a role in CF_4 mixes but does provide profile control in SF_6 mixes. Adding CHF_3 creates CF_2 radicals and forms a blocking C_xF_y layer on the Si surface. However, this film decomposes at much lower temperature than inorganic $\text{Si}_x\text{O}_y\text{F}_z$ film requiring relatively low ion bombardment and

reaction temperature to ensure the growing of a polymer film and vertical sidewall [6]. Passivation layers are important to achieving anisotropic etching behavior.

2.5.4 RIE Anisotropy

RIE is a highly anisotropic process. Directed energetic ion bombardment allows for relatively consistent etch directionality. Anisotropy is a description used to compare the amount of lateral to vertical etching and given by:

$$A = 1 - \frac{R_L}{R_V} \quad (5)$$

Where R_L and R_V are the lateral and vertical etch rates. When $A = 1$, the process is considered perfectly anisotropic. When $A = 0$ the lateral and vertical etch rates are identical. In RIE, etch gasses such as CF_4 lead to the deposition of fluoropolymer films which passivate sidewalls and improve anisotropy [4]. However, using fluorine-based plasmas have also shown undercutting, indicating a large chemical etch rate and a large degree of isotropic nature [8].

A critical component to achieving etch directionality and anisotropic profiling in Si is sidewall passivation which form etch inhibiting films to prevent mask undercutting. The bottom of the trench is exposed to ion bombardment and free from passivation allowing etching reactions to occur. The sidewalls receive no ion bombardment, allowing sidewall passivation to occur. This makes it possible to achieve etch directionality for etchant/substrate systems which normally exhibit isotropic etching characteristics [8].

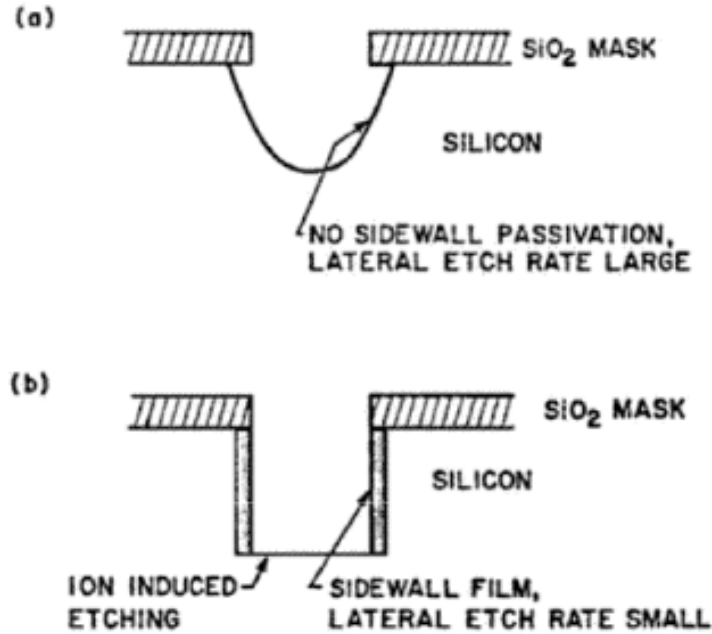


Figure 14: Concept of sidewall passivation mitigating mask undercutting [8].

The addition of O_2 as a reactive gas species is critical to the formation of protective sidewall film. However, the addition of sidewall forming gasses impacts etch rate and selectivity. The addition of 50% O_2 to SF_6 drops etch rate and selectivity ($\text{Si}:\text{SiO}_2$) by a factor of -5. [8].

As aforementioned in Section 2.5 important components of the RIE process are the transport of reactive species to the substrate surface and the removal of volatile reaction product. This makes etching trenches with submicron openings and high aspect ratios (depth:width) challenging. Chin *et al.* performed a study on relationship between etch rate and aspect ratio in submicron openings [35]. It was determined that etch rate decreases almost linearly as aspect ratio increases no matter the size of the opening.

For Si, high aspect ratios are possible for small features but the mean free path of ions and radicals within the etch plasma limit aspect ratio in large features ($>100 \mu\text{m}$).

Aspect ratio in features this size can be improved by using a low process pressure, diluting the plasma with a noble gas, and the addition of oxygen, which removes excess polymer formed during passivation. Unfortunately, these process manipulations also decrease etch selectivity. [11].

2.5.5 Etch Selectivity

Although plasmas are designed to target the Si surface, their products and by-products will also etch away the masking layer of PR. Etch Selectivity between two materials is defined as the ratio of their etching rates under identical etching conditions (6). A greater selectivity allows for deeper features to be etched into Si.

$$Selectivity = \frac{EtchRate_{material1}}{EtchRate_{material2}} \quad (6)$$

To etch deep, high aspect ratio trenches a relatively high degree of selectivity of Si:PR is required. Etch depth is limited to the ability of the PR to remain intact as a protective mask during etching. The maximum Si etch depth is the point in time at which the PR has been entirely etched away.

The difference in selectivity between two materials is attributed to rate differences in the adsorption, reaction, and desorption steps taking place at their surfaces[8]. These differences are caused by both physical and chemical etching mechanisms impacting the formation of volatile etch species. The goal of the selectivity studies described in Chapter III is to determine the RIE chemistries that provide the greatest selectivity and hence allow for the deepest maximum Si etch depth.

The etching of PR can be suppressed by [6]:

- Adding CF monomers from plasma gasses such as CHF_3 to absorb into the photoresist and compete with other radicals without etching.

- Cooling the substrate during etching.
- Lowering the bias voltage either by changing the reactor geometry, adding an insulating target or including an extra dummy wafer in the chamber.

This work only explores the effect of adding CHF_3 to limit PR etching. Opportunities for sample cooling and bias voltage manipulation in future studies are discussed in Section 5.5. It is important to note that substrate temperature is considered as an uncontrollable nuisance factor in this study. Over a period of time, the RF power and surface chemical reaction can cause the sample to heat up. Temperature change can add undesired energy to the process, bringing an additional process factor which is difficult to quantify when characterizing the etch rate, anisotropy, and selectivity of a given etch chemistry and chamber process factors. One method that can be used to cool the sample during RIE is the addition of Helium gas to the backside of the substrate. Air Force Institute of Technology (AFIT)'s Trion Minilock-Phantom III RIE has the capability, but is not currently equipped with helium cooling.

2.5.6 Si Crystal Effects on Etch Characteristics

As aforementioned in Section 2.4.2 Si crystallizes in the diamond structure, two interpenetrating face-centered cubic lattices.

An alternative way to depict the crystal structure of Si unit cell shown in Figure 9 is to visualize the Si lattice as a series of tetrahedral bonds. The atom is located in the center of each tetrahedron. Figure 15 shows the $\{111\}$, $\{100\}$ and $\{110\}$ planes of the Si lattice.

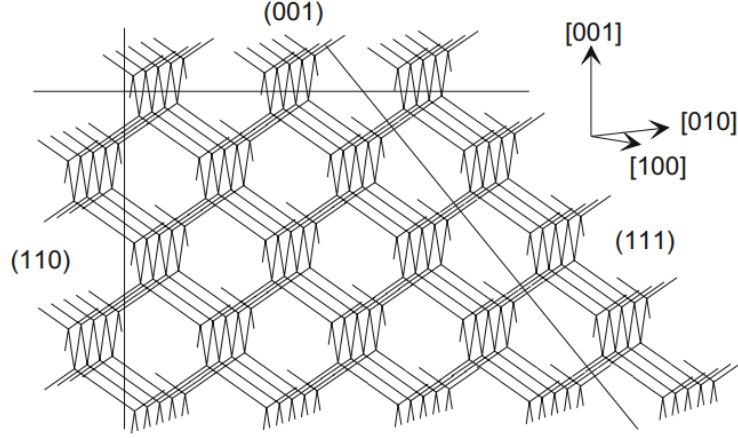


Figure 15: Silicon lattice tetrahedral bond configuration [9].

The etch rate of chemically driven processes is highly dependent on the crystallographic orientation of the surface in chemically driven etching processes. The surface crystal orientation of the wafer determines the number of free bonds on the surface. In order to separate an atom from the surface the bonds below the surface must be cut. Table 2 shows the number of back bonds that must be cut for each Si crystal surface orientation.

Table 2: Number of bonds below the surface for each silicon crystal surface orientation.

Crystal Surface Orientation	Bonds Below the Surface
{100}	2
{110}	2 (Avg)
{111}	3

On the {111} surface each atom has one free bond and three back bonds. As such, the etching of a {111} surface requires the greatest activation energy and is much slower than either the {110} or {100} surfaces. On the {100} surface each atom has two surface and two back bonds. On the {110} surface, a single atom can be separated by cutting three bonds but thereafter its neighbour only has one back bond, averaging

out to two bonds cut per atom. Additionally, atoms on the $\{100\}$ surface plane do not share bonds with each other. Separating one atom from the surface does not require the separation of its neighbors.

2.5.6.1 Doping Effects

The electronic doping properties of Si also affect etch rate. N-type Si etches faster than intrinsic which etches faster than p-type due to Coulombic effects. Coulomb attraction between donors and halogens enhances etch rates while Coulomb repulsion between donors and halogens inhibit Si etch rates. For dependence on etch rates dopant concentration in Si must be at least 10^{19} cm^{-3} [8].

2.6 Relevant Observations in the Problem Landscape

This chapter presented an overview topics most applicable to this thesis work. The crystal structure and chemical etching considerations of Si were discussed. DWL, its applicable characteristics, and ability to work around problems that arise on non-homogeneous PR layers are addressed. Finally an overview is provided of RIE, its etching process and mechanisms, and the characteristics which make it suitable to achieve relatively deep etches even without special processing techniques such as sidewall passivation and cryogenic cooling.

III. Methodology

3.1 Problem Approach

This chapter details the methodology used to realize the high resolution deep trench Reactive Ion Etching (RIE) on elevated rectangular surfaces to meet research objectives. First, studies were performed to determine the ideal etch chemistries and RIE chamber factor settings for high selectivity of silicon (Si) to Photoresist (PR). Next, the anisotropic behavior of those ideal RIE chemistries were qualitatively characterized. Finally, Direct Write Lithography (DWL) was performed on elevated rectangular silicon wafer surfaces as proof of concept. The intent and assumptions of this methodology are outlined and the investigated parameters, specific fabrication techniques, and testing approach are discussed. Figure 16 shows the three research avenues taken to intersect with the final research objective.

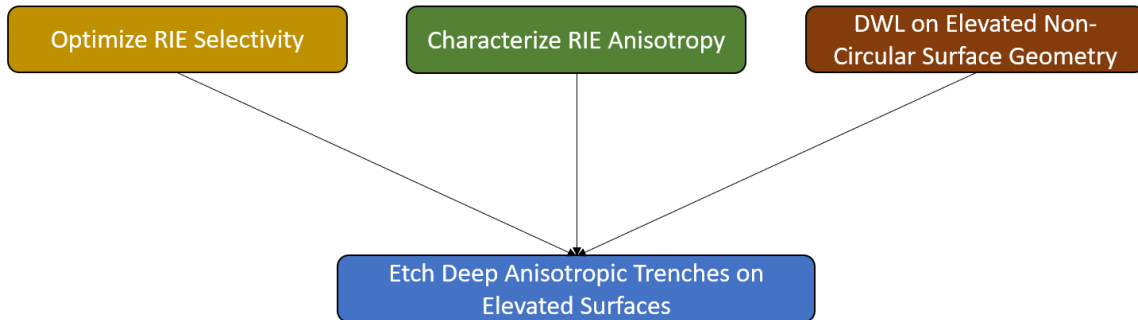


Figure 16: Selectivity experimental process overview.

3.2 Selectivity Studies

Multiple selectivity studies using two different etch chemistries, CF_4/O_2 and $\text{SF}_6/\text{CHF}_3/\text{O}_2$, and varying Trion Minilock-Phantom III RIE chamber factor settings were performed to confirm selectivity trends found in Chapter II and determine the most selective etch parameters.

Three 3^k factorial design selectivity studies were performed. At the time this work began, the Air Force Institute of Technology (AFIT) cleanroom did not have CHF_3 available. The first two selectivity studies focused on CF_4 and O_2 as the reactive gasses. Once CHF_3 became available, $\text{SF}_6/\text{CHF}_3/\text{O}_2$ was explored in the final selectivity study.

The first selectivity study was designed as a screening study to determine general trends in selectivity for a CF_4/O_2 reactive gas chemistry when varying RIE chamber parameters. A 3^2 factorial experiment was designed to test two different RIE factors: gas flow rate ratio and chamber pressure, each with three levels resulting in a total of nine different treatments. Etch time and RF Power remained the same throughout each treatment. This first study was performed on a 3" {100} n-type silicon test wafer masked with Shipley series 1818 (S1818) PR. After application via spin-coating, the S1818 was exposed with a 365 nm I-line UV radiation exposure source using a fused silica/chromium mask operating in hard contact mode and the PR pattern was developed away before etching.

The second selectivity study was a follow-on to the first. CF_4/O_2 was again used as the reactive gas chemistry. This study expanded upon the original two RIE factors, gas flow rate ratio and chamber pressure, based on selectivity trends determined in the first selectivity study. An additional factor, RF power, was added as well. Each factor had three levels. A 3^3 factorial experiment was designed containing 27 different treatments. In this study, each treatment was applied to three PR masks on three 3" {111} n-type wafer: S1818, bilayer resist (SF-11+S1818), and AZ 9260. A custom fused silica/chromium exposure mask was designed for this selectivity study for ease of analysis. After each PR was applied via spin-coating they were exposed with a 365 nm I-line UV radiation exposure source using a mask operating in hard contact mode (SF-11 was exposed to deep UV), and the PR pattern was developed away

before etching.

The third and final selectivity study examined $\text{SF}_6/\text{CHF}_3/\text{O}_2$ as the reactive gas chemistry. In this experiment four factors: SF_6 gas flow rate, CHF_3 gas flow rate, chamber pressure, and RF power were explored. O_2 gas flow rate and etch time were held constant through each treatment. A 3^{4-2} fractional factorial Taguchi orthogonal design was used to explore the selectivities of 9 different treatment combinations. Again, S1818, bilayer resist (SF-11+S1818), and AZ9260 were applied via spin-coating. In this experiment, DWL using the Heidelberg μPG101 was used to expose the PR.

The ultimate goal of these studies was to ascertain which treatments provide the highest selectivity, discover selectivity differences between the three PRs under the same treatment conditions, and determine the significance each RIE factor has for the selectivity of silicon to PR. These selectivity experiments involved six steps to create the experimental units, perform the RIE, and calculate the selectivity of each treatment. Figure 17 depicts the experimental process for determining etch selectivity.

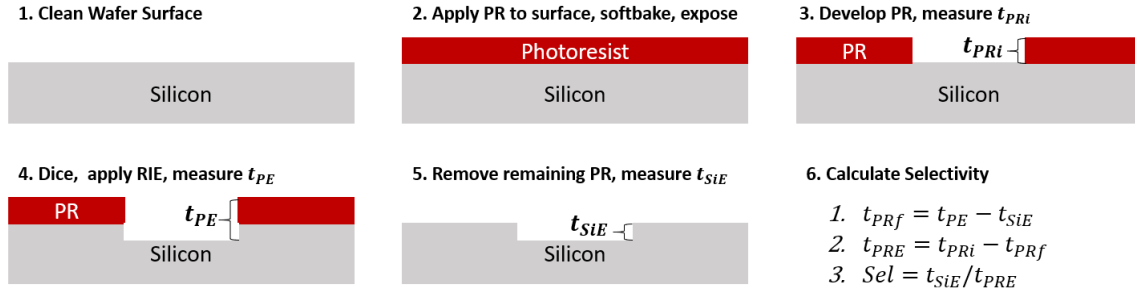


Figure 17: Selectivity experimental process overview.

Where:

- t_{Pri} is the initial thickness of the photoresist.
- t_{PE} is the measurement taken after etching. This measurement is the remaining photoresist and silicon etch depth.

- t_{SiE} is the silicon etch depth.
- t_{PRf} is the final thickness of the photoresist after etching.
- t_{PRE} is the thickness of photoresist etched away.
- Sel is the selectivity of the etch treatment (Silicon:Photoresist).

First, a layer of PR is spread onto a Si wafer, exposed, and developed. The thickness of the PR, t_{PRi} , is measured. Then, RIE treatments are performed on their respective units and a second measurement is taken giving the combined depth of silicon etched and remaining PR, t_{PE} . The remaining PR is removed and a final measurement is taken to determine the depth of silicon etched, t_{SiE} . Finally, the thickness of PR removed during etching, t_{PRE} , can be determined and the final selectivity of Si to PR. The ratio of Si to PR etched provides the selectivity of each treatment. The process shown in Figure 17 was used for all selectivity experiments. Etching was performed using the Trion III Phantom Minilock RIE-ICP system. Table 3 provides a summary of the three selectivity studies performed in this work.

Table 3: Summary of all selectivity studies performed in this work.

Study #	Exposure Method	Reactive Gas	RIE Factors	Factor Levels	# of Trts	PRs	Objective
1	Contact Mask	CF_4/O_2	1. Gas flow rate ratio ($CF_4:O_2$)	1:10, 1:13, 1:16	9	S1818	1. Determine trends in selectivity of RIE factors 2. Validate experimental design
			2. Chamber pressure (mTorr)	40, 50, 60			
2	Contact Mask	CF_4/O_2	1. Gas flow rate ratio ($CF_4:O_2$)	1:8, 1:18, 1:28	27	S1818 Bilayer AZ 9260	1. Determine RIE factors for optimal (Si:PR) selectivity 2. Characterize anisotropic behavior of RIE chemistries
			2. Chamber Pressure (mTorr)	80, 100, 120			
			3. RF Power (W)	70, 100, 130			
3	Direct Write Lithography	$SF_6/CHF_3/O_2$	1. SF_6 gas flow rate (sccm)	30, 40, 50	9	S1818 Bilayer AZ 9260	1. Determine RIE factors for optimal (Si:PR) selectivity 2. Characterize anisotropic behavior of RIE chemistries
			2. CHF_3 gas flow rate (sccm)	8, 14, 20			
			3. Chamber Pressure (mTorr)	100, 125, 150			
			4. RF Power (mTorr)	50, 100, 150			

3.2.1 General Experimental Design for Selectivity Studies

All selectivity studies utilize a variant of the 3^k factorial design. The 3^k factorial design is a factorial arrangement of k factors with three levels each. Factors and their interactions are denoted by the letters A, B, and C. The levels for each factor are the digits 0 (low), 1 (intermediate), and 2 (high). This experimental design yields 3^k treatment combinations and 3^k-1 degrees of freedom. Sum of squares can be determined for k main effects, each with two degrees of freedom; $(k/2)$ two-factor interactions, each with four degrees of freedom. If there are n replicates, there are $n3^k-1$ total degrees of freedom and $3^k(n-1)$ degrees of freedom for error [10].

The three basic principles of any experimental design are randomization, replication, and blocking. These principles are utilized whenever possible throughout this work. Additionally, repeated measurements are performed to provide additional certainty in results. Randomization assists in averaging out extraneous uncontrollable nuisance factors which may be present. Randomization is used in each selectivity study for assigning units to treatments and determining the order of treatments. Replication allows for estimate of experimental error to be calculated and help determine if observed differences are statistically significant. Replication is used in the first selectivity study, but not in the second and third due to time and material limitations. Finally, blocking is a design technique used to reduce or eliminate variability caused by nuisance factors. Blocking is utilized in the second selectivity study and discussed further in Section 3.2.3.2.

3.2.2 Initial CF₄/O₂ RIE Selectivity Study

The goal of the first selectivity experiment was to determine the RIE factors which had the greatest impact on selectivity of the CF₄/O₂ reactive gas species and determine any trends in selectivity related to factors and their levels. The 3^2 system is

the simplest of the 3^k factorial experiments and was chosen as the design for the initial selectivity screening study. The 3^2 design has two factors each with three levels for a total of 9 treatment combinations. Figure 18 depicts the treatment combinations in a 3^2 design.

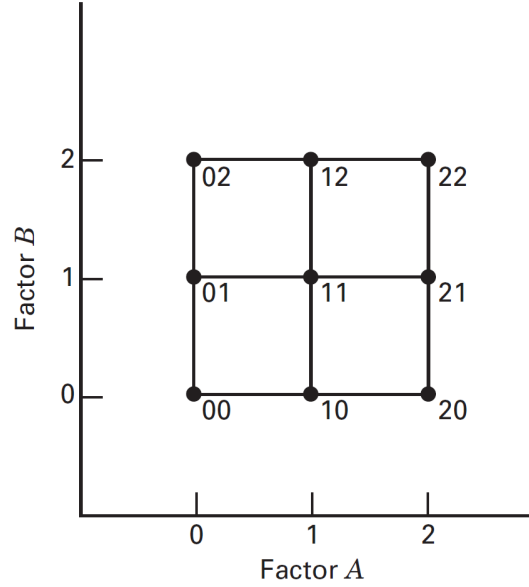


Figure 18: Treatment combinations used in the initial CF_4/O_2 RIE selectivity study [10].

Here, the two factors are denoted by the letters A and B and levels are denoted by 0 (low), 1(intermediate), and 2(high). In Figure 18 the nine treatments are each represented by two digits. The first digit corresponds to the level of factor A and the second corresponds to the level of factor B. For this initial selectivity study Gas Flow Rate Ratio ($\text{O}_2 : \text{CF}_4$) was selected as factor A and Chamber Pressure was selected as factor B. Table 4 shows the factors and experimental levels chosen in this study.

Table 4: Assignments of factors and levels in the initial CF₄/O₂ RIE selectivity study.

Levels	Factor A: Gas Flow Rate Ratio (O ₂ : CF ₄) sccm	Factor B: Chamber Pressure (mTorr)
0 (low)	3 : 30(1 : 10)	40
1 (intermediate)	3 : 39(1 : 13)	50
2 (high)	3 : 48(1 : 16)	60

From Table 4 and referencing Figure 18, the treatment "01" corresponds to a gas flow rate ratio of (1 : 10) and a chamber pressure of 50mTorr. Letting x_1 represent Gas Flow Rate Ratio (Factor A) and x_2 represent RIE Chamber Pressure (Factor B) the following regression model can be developed as shown in Equation 7 relating the response y (Selectivity) to x_1 and x_2 .

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{12} x_1 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \epsilon \quad (7)$$

The third factor level allows the relationship between the response and design factor to be modeled as quadratic, however, there are important considerations which must be taken into account with a 3^k design. Response surface designs are much more effective if a quadratic relationship between the response and the design factor is anticipated, a 2^k design augmented with center points is a much more useful tool if the relationship is expected to have curvature, and a split-plot should be considered if the interaction of each factor is expected to have a significant effect[10]. However, previous research anticipated a linear relationship between the chosen factors and selectivity [36]. Additionally, factor interactions were not expected to have significant effects, therefore a 3^k experimental design was utilized.

In a 3^2 design, the sums of squares for A, B, and AB can be computed using usual methods for factorial designs. Each main effect can be represented by a linear and quadratic component, each with a single degree of freedom. Table 5 shows the

ANOVA for a two factor fixed effects model [10].

Table 5: Equations used to solve for an ANOVA table for the initial CF₄/O₂ RIE selectivity study [10].

Source of Variation	Sum of Squares	DOF	Mean Square	Expected Mean Square	F_0
A	SS_A	2	MS_A	$\sigma^2 + \frac{bn}{a-1} \sum \tau_i^2$	$F_0 = \frac{MS_A}{MS_E}$
B	SS_B	2	MS_B	$\sigma^2 + \frac{an}{b-1} \sum \beta_j^2$	$F_0 = \frac{MS_B}{MS_E}$
AB	SS_{AB}	4	MS_{AB}	$\sigma^2 + \frac{n}{(a-1)(b-1)} \sum (\tau \beta)_{ij}^2$	$F_0 = \frac{MS_{AB}}{MS_E}$
Error Total	SS_E	ab(n-1)	MS_E	σ^2	
	SS_T	abn-1			

The equations shown in Table 5 are what statistical software packages use when populating the ANOVA table for a general 3² full factorial design.

3.2.2.1 Design of Experiment in the Initial CF₄/O₂ RIE Selectivity Study

First, the 3'' {100} n-type silicon wafer surface is cleaned. Then, an ≈ 1900 Å layer of S1818 PR is spun onto the wafer. To drive out the solvent from the PR, a soft bake of the coated wafer is ran at 110°C for 2 min. Next, the wafer is irradiated under 365 nm I-line UV radiation for 6 s under a chrome mask to create a pattern in the PR. For the first CF₄/O₂ selectivity study a mask is utilized to pattern an array of rectangles approximately 200 μm × 400 μm across the entire wafer. A post-bake is done at 110°C for 2 min to remove any remaining solvent and the wafer is placed in a buffered oxide etch solution to develop the pattern. Figure 19 shows the wafer after the rectangular array pattern development.

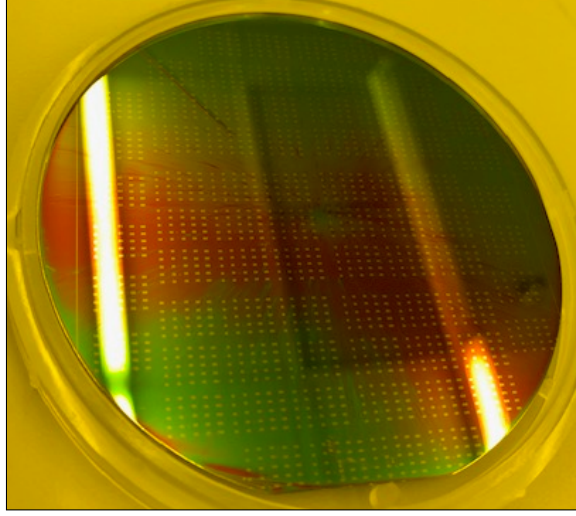


Figure 19: Wafer patterned with an array of rectangles in the initial CF_4/O_2 RIE selectivity study.

A profilometer was used to take step-height measurements to confirm the expected PR thickness t_{PRi} . The arithmetic mean of the profilometer measurements taken was $1.9119 \mu\text{m}$, close to the expected value of $1.8 \mu\text{m}$ based on the spin-coating process used and . Differences between actual and expected values can be attributed to profilometer measurement, variations and differences in storage and clean room conditions which may affect PR viscosity, and the mechanical system used to spin-coat the PR.

3.2.2.2 Unit Assignment in the Initial CF_4/O_2 RIE Selectivity Study

To create the required units for the study the masked wafer was diced into 32 roughly equivalent pieces as shown in Figure 20. For this experiment three replicates were used for each of the nine treatments, resulting in 27 total units. To minimize confounding effects, each unit is diced from the same wafer.

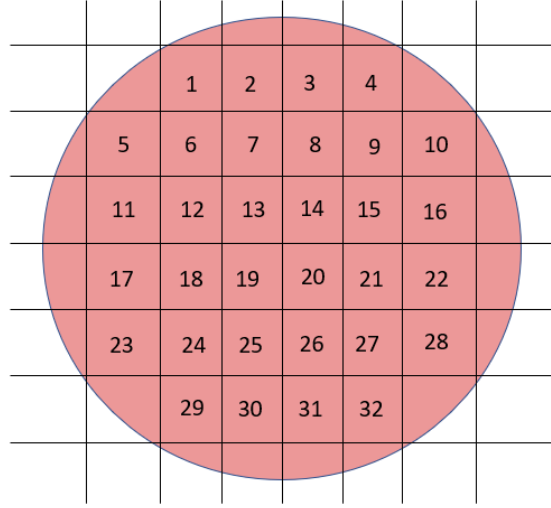


Figure 20: Depiction of wafer design diced into 32 equivalent pieces.

Each unit was diced by hand using a diamond tip pen and straight edge. The exact size and shape of each piece was not a concern as long as there were enough measurable rectangles exposed. Each of the diced wafers were stored in an order corresponding to their location as shown in Figure 20. To assign each unit to a treatment, a random permutation MATLAB function was used to select nine groups of three units each. Shown below in Table 6 is the final treatment assignment for each unit.

Table 6: Unit assignments by treatment for the initial CF_4/O_2 RIE selectivity study.

	Gas		
	Flow Ratio ($\text{O}_2:\text{CF}_4$)		
Chamber Pressure	A (1:10)	B (1:13)	C (1:16)
1 (40 mTorr)	2, 20, 6	23, 25, 9	3, 15, 28
2 (50m Torr)	26, 11, 5	29, 17, 7	14, 30, 8
3 (60m Torr)	21, 13, 4	12, 31, 27	22, 18, 10

Five units (1, 16, 19, 24, 32) were unused in the experiment to ensure balanced replication. Test silicon wafers are relatively cheap and disposable so design optimization techniques were not required in this study. The experimental units were then organized and sorted to match their treatment assignments from Table 6 as shown in Figure 21.

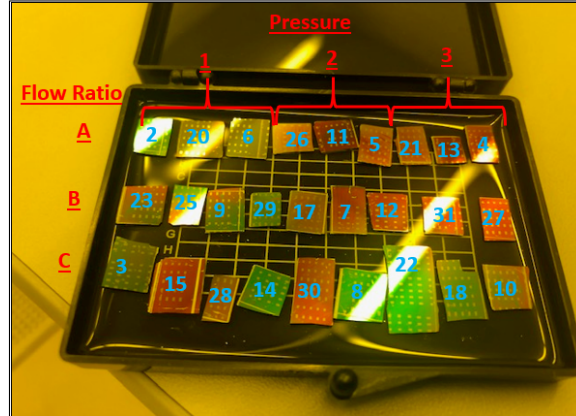


Figure 21: Wafer pieces assigned to each treatment after sorting in the initial CF_4/O_2 RIE selectivity study. Red indicates treatments and blue indicates unit number.

Figure 21, how the units were organized and tracked throughout the experiment, is just the transpose of Table 6. Tracking and organizing each unit throughout the duration of the study was a challenge addressed by creating a custom mask for follow-on studies as described in Section 3.2.3.1 and shown in Figure 22.

With each of the 27 units matched to one of the nine treatments (3 replicates per treatment), RIE is performed on each unit. Treatments are shown in Table 7. Each etch was performed at a power setting of 100 W for 10 min.

RIE treatments were performed with all three replicates in the chamber at once to reduce the overall time of the experiment and eliminate a potentially confounding error associated with the RIE machine maintaining exact chamber settings between runs. After each etch treatment is applied to its respective units, a profilometer is used to take four different step height measurements on each unit.

To ensure the same features (rectangles) were measured throughout the first CF_4/O_2 selectivity study, the two features adjacent to the "beam length" alignment mark closest to the center of each piece of wafer were measured. Repeated measurements were performed to account for depth measurement variability from both the features and the measurement device itself. A total of 4 step-height measurements were taken at each step for each unit. Two step-height measurements were taken and the wafer was then rotated 90° for two additional step-height measurements on an adjacent edge of the same features.

After measurements were completed, the PR is cleaned using a 30 second acetone, methanol, and DI water rinse. The measurement process is then repeated again to determine the etch depth of the silicon. After taking and averaging the step-height measurements on each unit taken after PR development, etching, and PR removal, the selectivity for each treatment and unit was determined using Equation 8.

$$\begin{aligned}
t_{PRE} - t_{SiE} &= t_{PRf} \\
t_{PRi} - t_{PRf} &= t_{PRE} \\
Selectivity &= \frac{t_{SiE}}{t_{PRE}}
\end{aligned} \tag{8}$$

Where the variables are pictured in Figure 17 and defined earlier in Section 3.2.2.

3.2.3 Follow-on CF₄/O₂ RIE Selectivity Study

The purpose of this study was to confirm selectivity trends determined in the initial selectivity study, add an additional RIE factor to be studied, and determine the RIE factor settings which yielded the highest selectivities using CH₄ and O₂ as the reactive gas species. This time, a 3³ factorial design was performed. In this experiment, RF power was added as a third factor C, also with three levels. The 3³ design has three factors each with three levels for a total of 27 treatment combinations.

As in the initial selectivity study: Factor A is Gas Flow Rate Ratio (O₂:CF₄), Factor B is Chamber Pressure (mTorr), and the additional Factor C is RF Power (W). Each factor has three levels: 0 (low), 1 (intermediate), and 2 (high). Table 7 shows the factors and levels chosen in this study.

Table 7: Assignments of factors and levels for the follow-on CF₄/O₂ RIE selectivity study.

Levels	Factor A: Gas Flow Rate Ratio (O ₂ : CF ₄) sccm	Factor B: Chamber Pressure (mTorr)	Factor C: RF Power (W)
0 (low)	3 : 24(1 : 8)	80	70
1 (intermediate)	3 : 54(1 : 18)	100	100
2 (high)	3 : 84(1 : 28)	120	130

Again, CF₄ and O₂ were utilized as the reactive gas species. From Table 7, the example treatment "012" corresponds to a gas flow rate ratio of (1 : 10), a chamber

pressure of 50mTorr, and an RF power of 130 W. Figure 22 shows the mask that was developed to aid with unit organization and profilometer measurements after etching.

3.2.3.1 Experimental Design for Follow-on CF_4/O_2 RIE Selectivity Study

To aid with analysis in the second CF_4/O_2 selectivity study a custom mask was developed. Figure 22 shows the mask design and exposure pattern.

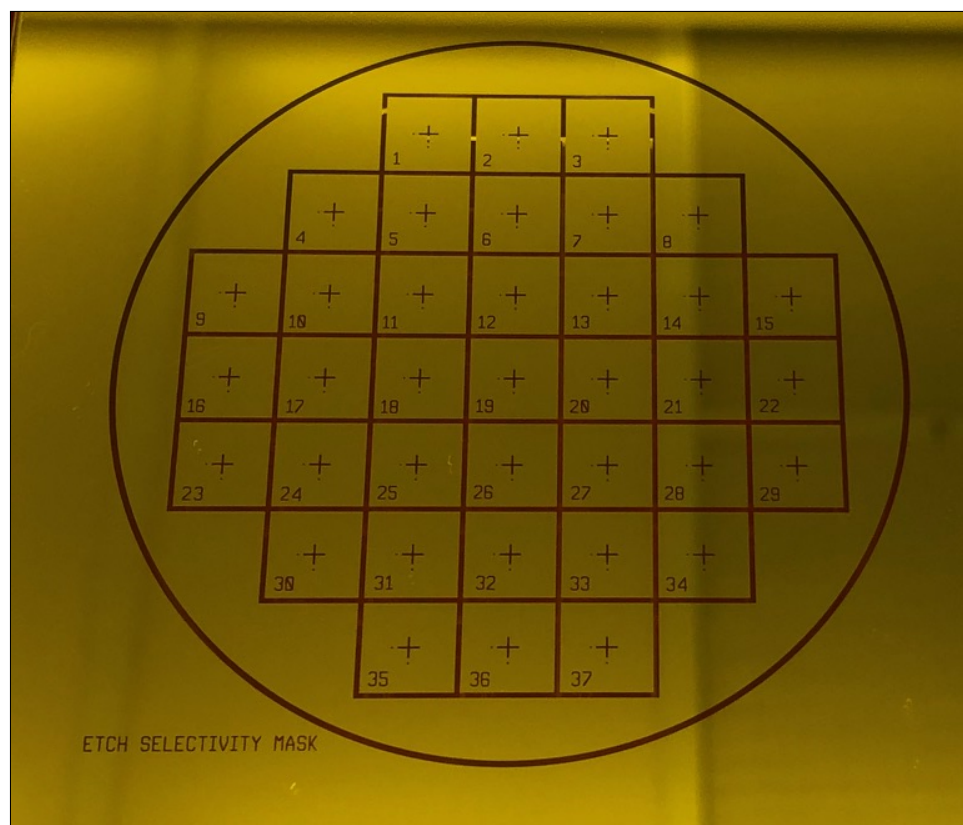


Figure 22: Mask design for the follow-on CF_4/O_2 RIE selectivity study.

Each unit was individually labeled. This allowed for units to be easily assigned, organized, measured, and tracked throughout the study. The primary feature was two intersecting beams in the shape of a cross, each $200 \times 2000 \mu\text{m}$. This design was done to provide 4 convenient locations to make profilometer measurements using

the measurement process depicted in Figure ???. The same experimental procedure presented in Section 3.2.2 was performed.

Due to limited material resources, and to determine if RIE factor trends applied to various crystallographic wafer orientations, this study was performed on {111} n-type wafers. The chemical etch rate of the {111} surface orientation is slower than either {110} or {100} as discussed in Section 2.5.6. Thus, this study on {111} n-type wafers provided a "worst case" Si to PR etching selectivity study. It can be assumed that applying these same treatments to {110} or {100} surface orientations will result in equivalent or improved selectivity results.

Three PRs of varying composition and thickness were applied via spin coating to the surfaces of three wafers. Each individual unit's PR thickness was measured and tabulated. Table 8 shows the PRs and the arithmetic mean of the measured thicknesses for all 27 units of each PR used within the study. Also included are the spin speed settings used for spin-coating.

Table 8: Photoresists used in the follow-on CF_4/O_2 RIE selectivity study, average unit thickness, and spin speed and soft bake settings.

Photoresist	Thickness (μm)	Spread Speed & Time	Spin Speed & Time	Softbake Temperature & Time
Shipley 1818	1.914	5 sec @ 500 rpm	30 sec @ 4000 rpm	120 sec @ 110°C
Bilayer (SF-11)†	3.350*	5 sec @ 500 rpm	30 sec @ 4000 rpm	120 sec @ 200°C
AZ 9260	11.410	5 sec @ 300 rpm	60 sec @ 2400 rpm	165 sec @ 110°C

*This value includes the thickness of the S1818 spun on the bilayer resist under the same conditions listed in the table. †The spin speed and softbake settings listed in this row are for SF-11 only.

After optimal exposure settings were determined, AZ 9260 was exposed using a 365 nm I-line UV radiation exposure source and developed with AZ 726 MIF developer. For the bilayer resist, SF-11 was applied to the wafer surface first followed by S1818 with the settings listed above. The S1818 was first exposed using a 365 nm I-line UV radiation exposure source and mask shown in Figure 22 operating in con-

tact mode. The exposed pattern was developed using 351B developer, opening up the desired pattern on the SF-11. Then, the remaining S1818 acted as a mask while the entire wafer was exposed to a deep Ultraviolet (UV) exposure source for 200 sec and developed in 101A developer. Initial intentions were to then use 351B developer to remove the remaining S1818 and leave only SF-11 on the surface of the wafer. However, the S1818 did not develop away in sufficient time to remain selective and SF-11 was removed from the surface. Therefore, since the overall goal of this research was achieving a deep anisotropic etch, the selectivity of the bilayer resist, with both S1818 and SF-11 was studied. Additionally, assuming that the entire layer of S1818 would not be etched away during the study, this allowed for comparison of S1818 etch selectivities at different thicknesses.

3.2.3.2 Blocking to Eliminate Nuisance Factors in the Follow-on CF_4/O_2 RIE Selectivity Study

Blocking is one of the three basic principles of any design of experiment (DOE). Blocking is used to reduce or eliminate experimental variability caused by nuisance factors and improves precision with which comparisons among the factors of interest are made [10].

In this case, 27 different etch treatments were performed. During RIE, the volatile reactive species removed from the substrate and PR is sometimes not flushed from the chamber and can be deposited on the chamber walls and components. This material can unintentionally be redeposited or reduce the percentage of reactive gas species available for etching. After a number of etches this buildup can become significant impacting the etch rate and selectivity of subsequent etches. Therefore, an O_2 "flush" of the chamber must be periodically run to clear away any undesired chamber depositions. To mitigate the buildup of chamber deposition as a nuisance

factor, and allow for an O₂ system cleaning to be performed periodically throughout the experiment, this selectivity study was split into three blocks and chamber clean was run between each block. Three blocks of 9 treatments each were generated by confounding the AB^2C^2 component of the three factor interaction and using the corresponding defining contrast as shown in 9.

$$L = x_1 + 2x_2 + 2x_3 \quad (9)$$

Using the defining contrast, treatment assignments to each block were defined as shown in 23.

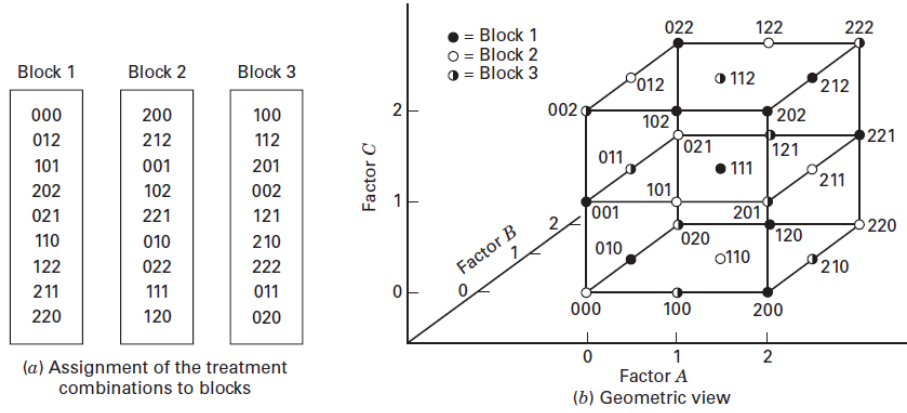


Figure 23: Treatments in three blocks with AB^2C^2 confounded for the follow-on CF₄/O₂ RIE selectivity study[10].

The order of treatments performed within each block was randomized and one wafer unit from each PR was randomly assigned to each treatment using MATLAB's random permutation function. Table 9 shows the unit assignments for each PR and the treatments assigned to each block.

Table 9: Assignment of units and treatment blocks in the follow-on CF₄/O₂ RIE selectivity study.

	Factor A: Gas Flow Ratio (O ₂ :CF ₄)								
	0 (1:8)			1 (1:18)			2 (1:28)		
Factor C: Power	0 (70mW)	1 (100mW)	2 (130mW)	0 (70mW)	1 (100mW)	2 (130mW)	0 (70mW)	1 (100mW)	2 (130mW)
Factor B: Pressure	0 (70mW)	1 (100mW)	2 (130mW)	0 (70mW)	1 (100mW)	2 (130mW)	0 (70mW)	1 (100mW)	2 (130mW)
0 (80mTorr)	000	001	002	100	101	102	200	201	202
S1818	26	31	7	5	10	25	3	18	8
Bilayer (SF11+S1818)	7	19	36	33	20	12	28	2	24
AZ9260	34	4	1	14	2	30	27	3	5
1(100mTorr)	010	011	012	110	111	112	210	211	212
S1818	30	14	9	36	1	2	28	16	33
Bilayer (SF11+S1818)	0	6	23	29	11	5	8	21	26
AZ9260	26	29	32	23	28	17	31	20	25
2(120mTorr)	020	021	022	120	121	122	220	221	222
S1818	6	29	21	13	19	34	20	24	17
Bilayer (SF11+S1818)	35	31	9	32	17	37	1	3	4
AZ9260	7	24	19	36	12	11	13	6	33

Where: # = Unit number, # = Treatment combination, # = Block 1, # = Block 2, # = Block 3

As can be seen in Table 9, confounding provides well-balanced treatment assignment between blocks. Before the experiment began, and between each block of treatments, a 10 minute chamber clean was performed using an O₂ gas flow rate of 60 SCCM and RF power of 100 W.

3.2.3.3 Qualitative Analysis of CF₄/O₂ RIE Anisotropy using DWL

The ultimate research goal of this work was to characterize the anisotropic behavior of highly selective RIE chemistries. Previous work up to this point had focused only on determining the CF₄/O₂ RIE factor settings that provided the highest selectivities. Selectivity determines the maximum etch depth that can be reached before the protective masking layer of PR is removed from the surface. Therefore, higher selectivity leads to deeper etches and greater opportunity to characterize anisotropy.

However, the first two selectivity studies did not generate trenches deeper than 4μm. At this depth it is difficult to characterize the anisotropic behavior of the etch.

Therefore, an additional study was required to generate deep trenches which could be characterized.

The most selective CF_4/O_2 RIE treatments were tabulated. Using the measurements taken during the follow-on CF_4/O_2 RIE selectivity study, the PR and Si etch rates were determined. Using the assumption that these etch rates would remain constant independent of etch time, the maximum etch depth, and the time to reach maximum etch depth was determined for the most selective CF_4/O_2 RIE treatments. Based on these assumptions, an additional CF_4/O_2 RIE study was developed to use the most selective chemistries to etch deep trenches in order to characterize anisotropic behavior.

Unfortunately, due to a lack of CF_4 available, this final study designed to characterize the anisotropic behavior of highly selective RIE chemistries with CF_4/O_2 could not be performed. Although CHF_3 was not available when this work began, by the time this final study was designed, CHF_3 was now available for use. This provided the opportunity to instead characterize the selectivity and anisotropic behavior of RIE with $\text{SF}_6/\text{CHF}_3/\text{O}_2$.

3.2.4 $\text{SF}_6/\text{CHF}_3/\text{O}_2$ RIE Selectivity Study

To optimize selectivity and perform a qualitative characterization of etch anisotropy for RIE using $\text{SF}_6/\text{CHF}_3/\text{O}_2$ as the reactive gas species, an experimental design was developed leveraging the analysis of the first two CF_4/O_2 selectivity studies and additional background research [37].

This study examined the RIE selectivity and anisotropy of Si to S1818, bilayer (SF-11+S1818), and AZ9260 PR using $\text{SF}_6/\text{CHF}_3/\text{O}_2$ as a reactive gas species and DWL as the exposure tool.

As in the second selectivity study, PRs were applied to a 3" {111} n-type wafer

using the same procedure and settings outlined in Section 3.2.3.1 and Table 8. DWL was performed using the Heidelberg μ PG101 Micro Pattern Generator with an $1\mu\text{m}$, 375 nm exposure beam source. Shipley 1818 and AZ9260 are both capable of absorbing 375nm wavelength and thus well suited for DWL using this exposure source. Figure 26 shows the design exposed using DWL onto each PR.

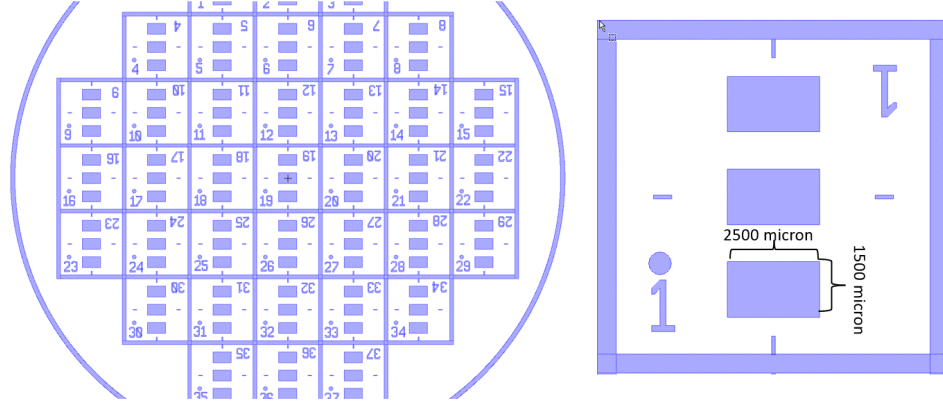


Figure 24: Direct write design for the $\text{SF}_6/\text{CHF}_3/\text{O}_2$ RIE selectivity study.

Various batch exposures with different power settings were performed to determine the optimal exposure settings for both S1818 and AZ 9260. Figure 25 shows the developed DWL design using direct write settings at 50mW, 1x1 stage settings, and a 10% pulse duration on S1818 PR.



Figure 25: DWL exposure design after development of Shipley 1818 photoresist on a 3" {111} n-type wafer used in the $\text{SF}_6/\text{CHF}_3/\text{O}_2$ RIE selectivity study.

Legtenberg *et al.* studied the anisotropic RIE of Si using $\text{SF}_6/\text{CHF}_3/\text{O}_2$ mixtures and used as a baseline for determining factor levels [37]. Test etches were performed to confirm the viability of the factors and levels selected. The factors and levels used in this selectivity study are shown in 10.

Table 10: Factors and Levels for the $\text{SF}_6/\text{CHF}_3/\text{O}_2$ RIE Selectivity Study.

Levels	Factor A: SF_6 Gas Flow Rate (sccm)	Factor B: CHF_3 Gas Flow Rate (sccm)	Factor C: Chamber Pressure (mTorr)	Factor D: RF Power (W)
0 (low)	30	8	100	50
1 (intermediate)	40	14	125	100
2 (high)	50	20	150	150

For the selectivity aspect of this study a 3^{4-2} fractional factorial Taguchi orthogonal design was used to explore the selectivities of 9 different treatment combinations.

This model assumes no effects between individual factors. Level settings among factors occur an equal number of times, providing valuable information regarding their impact on selectivity while greatly reducing the overall number of treatments required. Four RIE chamber factors: SF₆ gas flow rate, CHF₃, chamber pressure, and RF power each with three levels were analyzed. O₂ gas flow rate and etch time were held constant. Table 11 shows the nine treatments applied and their associated factor settings.

Table 11: Treatments for the SF₆/CHF₃/O₂ RIE Selectivity Study.

Treatment	SF ₆ Gas Flow Rate (sccm)	CHF ₃ Gas Flow Rate (sccm)	O ₂ Gas Flow Rate (sccm)	Chamber Pressure (mTorr)	RF Power (W)	Etch Time (min)
1	30	8	3	100	50	12/24
2	30	14	3	125	100	12/24
3	30	20	3	150	150	12/24
4	40	8	3	125	150	12/24
5	40	14	3	150	50	12/24
6	40	20	3	100	100	12/24
7	50	8	3	150	100	12/24
8	50	14	3	100	150	12/24
9	50	20	3	125	50	12/24

In this study, two units of each PR mask were assigned to a treatment. After 12 minutes of a respective RIE treatment, one unit of each PR was removed. The remaining units received the same RIE treatment for another 12 minutes. This created two data points for each PR and treatment which could be used for anisotropic characterization. The selectivities presented in Section 4.2.3 were calculated from the units etched for 24 minutes.

3.3 Qualitative Analysis of $\text{SF}_6/\text{CHF}_3/\text{O}_2$ RIE Anisotropy using DWL

The same units used in the $\text{SF}_6/\text{CHF}_3/\text{O}_2$ RIE selectivity study were analyzed for anisotropic characterization. The exposure design in Figure 26 is similar to the etch selectivity study mask design used in Section 3.2.3, but modified to allow for easy analysis of etch anisotropy. Three rectangles $1500 \times 2500 \mu\text{m}$ are aligned on each unit providing three opportunities to analyze anisotropy on each unit. Alignment marks are placed to assist with cross-sectioning. Each unit is labelled with a number on both sides with an additional mark added on top of one number to allow for the unit to be easily tracked throughout the analysis process and after cross-sectioning. Anisotropy and final etch depth were determined using the process outlined in Figure 26.

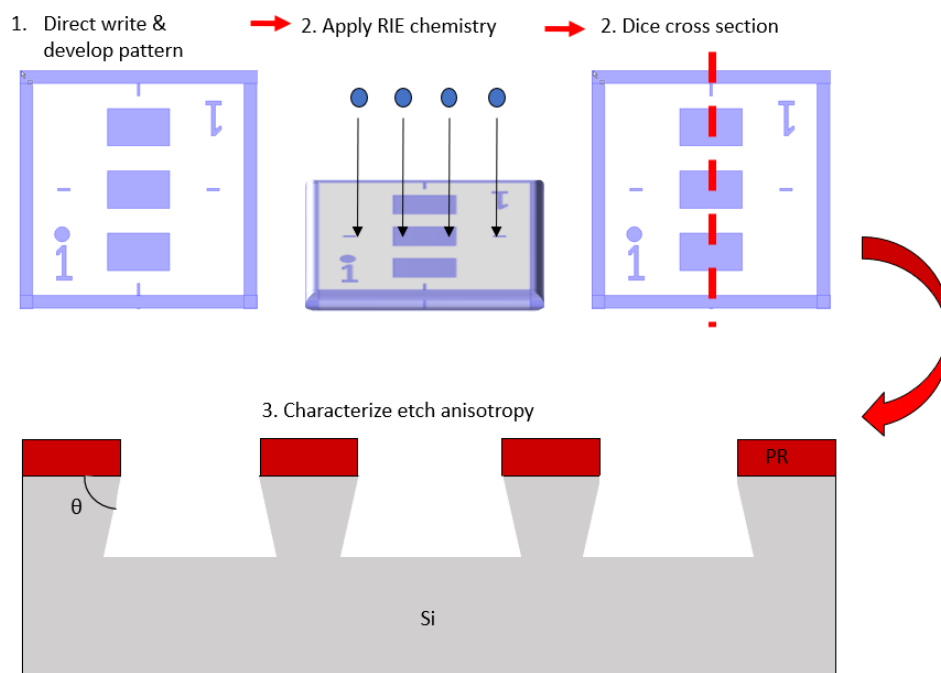


Figure 26: Direct write etch study process

3.4 DWL for RIE on Elevated Rectangular Substrates

In order to realize the overall research goal of this work a proof of concept study was performed to test the Heidelberg μ PG 101 mask writer's ability to write on elevated rectangular surfaces. First, test wafers were diced into roughly equivalently sized rectangles with dimensions ranging from 4000 to 8000 μm . Each test wafer thickness ranges from 375 to 500 μm . Rectangles are sorted and organized based on relative size to ensure stack uniformity. Stacks of wafers, 2, 3, and 4 high were generated. S1818 PR was used as a glue between wafer layers then baked for 2 minutes at 110 C to ensure bonding. The top layer was spun separately with the photoresist (S1818, SF-11, or AZ 9260), softbaked, then glued as the top layer for direct write using the Heidelberg μ PG 101 mask writer. The estimated heights of each stack are listed below:

- Single Stack: 750 to 1000 μm height
- Double Stack: 1125 to 1500 μm height
- Triple Stack: 1500 to 2000 μm height

Figure 27 depicts the wafer stacks and their estimated height.

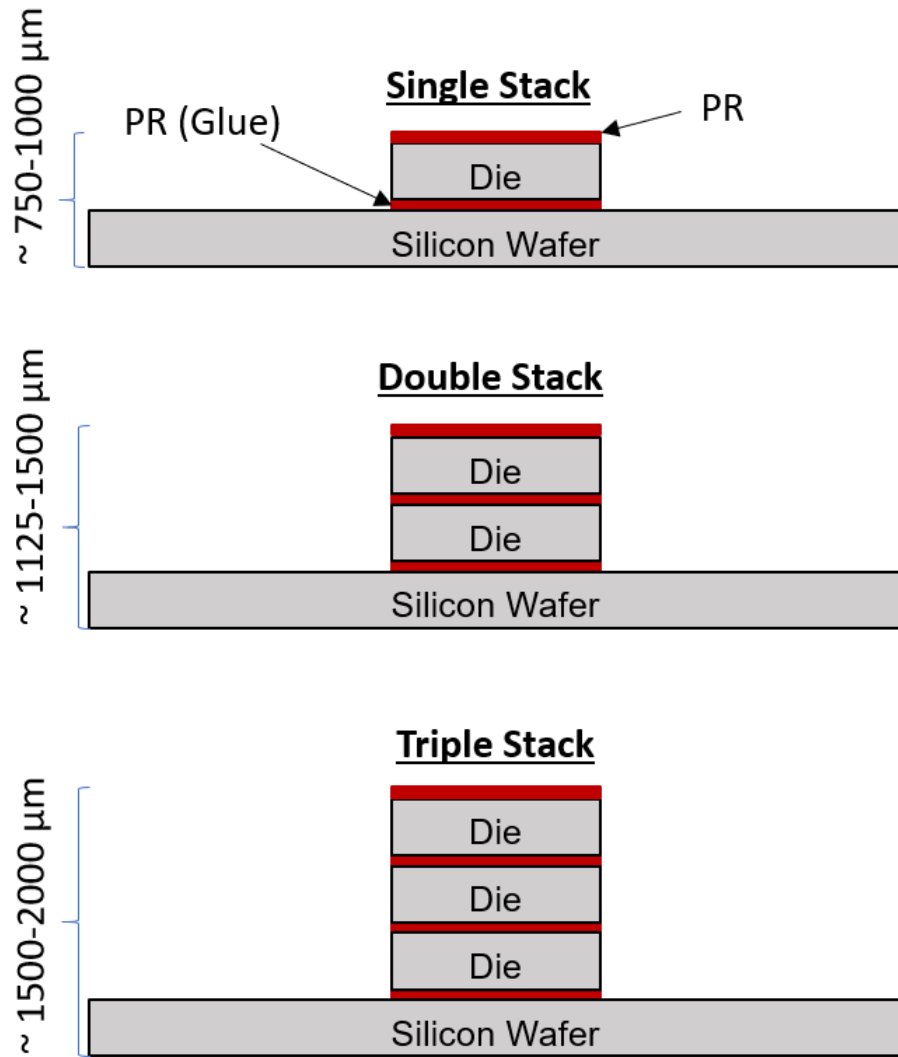


Figure 27: Single, double, and triple stacked wafer developed for elevated direct write proof of concept.

Initial testing was done on a single wafer to determine the Heidelberg μPG 101 settings which provided the optimum exposure for both S1818 and AZ 9260. After each direct write the wafer was treated in developer and analyzed. Figure 28 shows the simple 200 x 2000 μm cross written for each test.

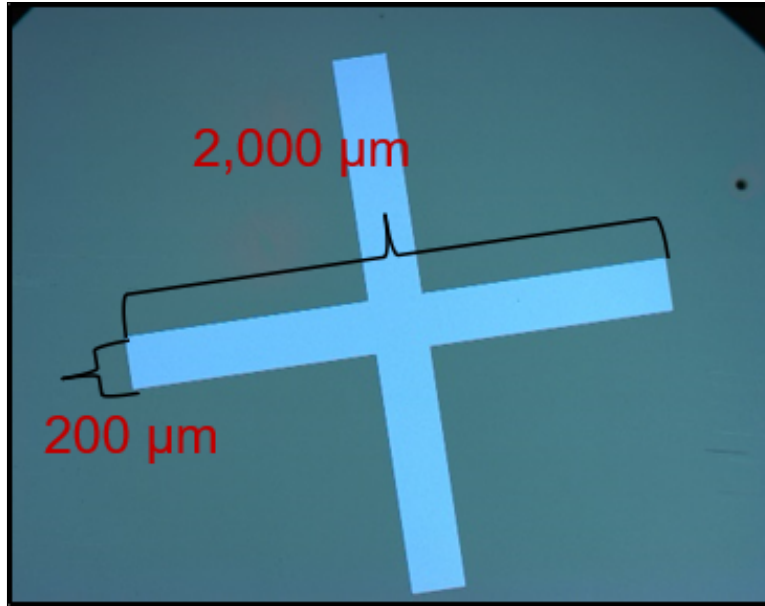


Figure 28: Exposure pattern for wafer stack direct write testing. Image of single wafer direct write on Shipley 1818 photoresist after development.

Once optimum exposure settings were dialed in, stack testing was done progressively, starting with the single stack and proceeding through the triple stack. The top layer of the stack was spun separately with the desired photoresist. Intermediary wafers were adhered together by spreading S1818 between each layer and applying 110°C softbake to cure. Figure 29 depicts a direct write exposure and development on a single stack elevated surface.

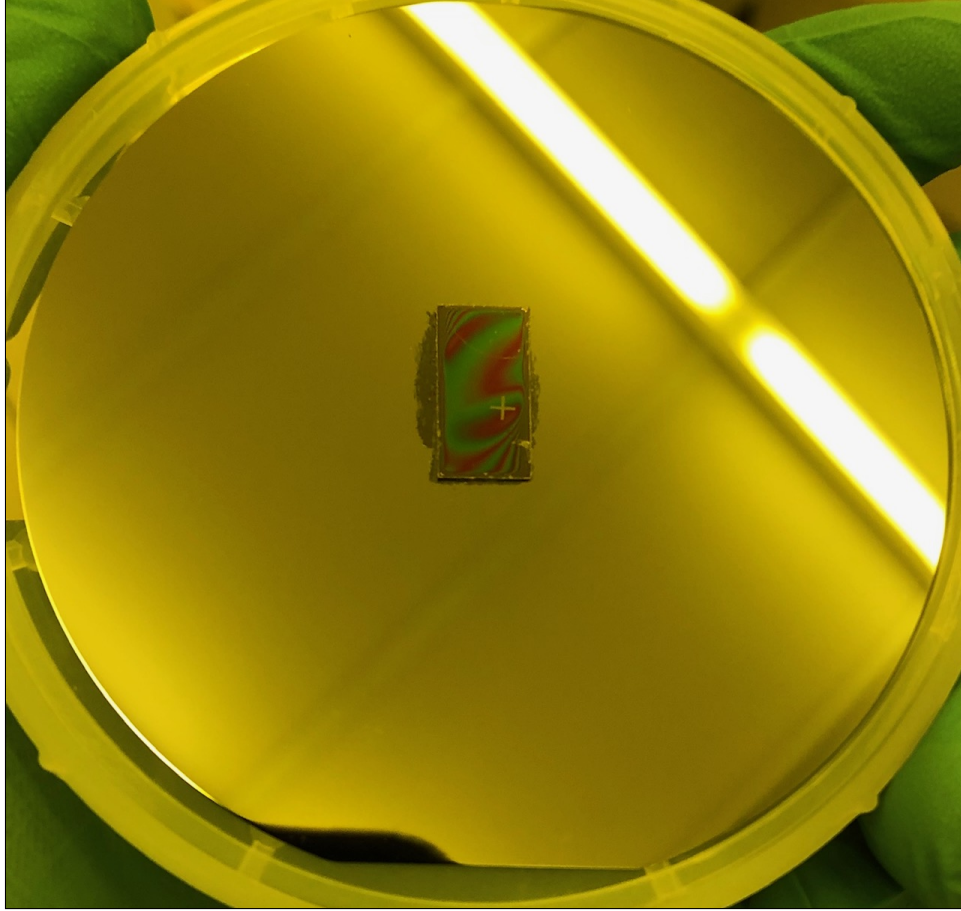


Figure 29: Direct write exposure on elevated wafer surface

Each direct write exposure on elevated stacks was successful. The Heidelberg μ pg101 appears to have no limitation for focusing on elevated surfaces relative to those of chips and packages. The ultimate height limit for exposure using the Heidelberg μ pg101 was not explored due to concern with causing severe damage to the machine.

3.4.0.1 DWL Feature Resolution on Elevated Rectangular Surface

Among the three photoresists studied throughout this work, AZ 9260 offers the highest potential to achieve deep, high resolution etch profiles. AZ 9260 is relatively viscous while maintaining low optical absorption allowing for thicker layers to be successfully applied and exposed. Layers ranging from 9 to 38 μ m thick can be spun

onto a substrate surface with standard processing techniques.

First, an approximately $10\text{ }\mu\text{m}$ layer of AZ 9260 was spun onto a square substrate. Then, using the same process outlined in Section 3.4, a 3 stack wafer was generated. To determine the feature resolution capabilities of the Heidelberg Direct Write system a design including a variety of shapes, sizes, and spacing was created in L-Edit. Figure 30 shows a zoomed out view of the final design layout.

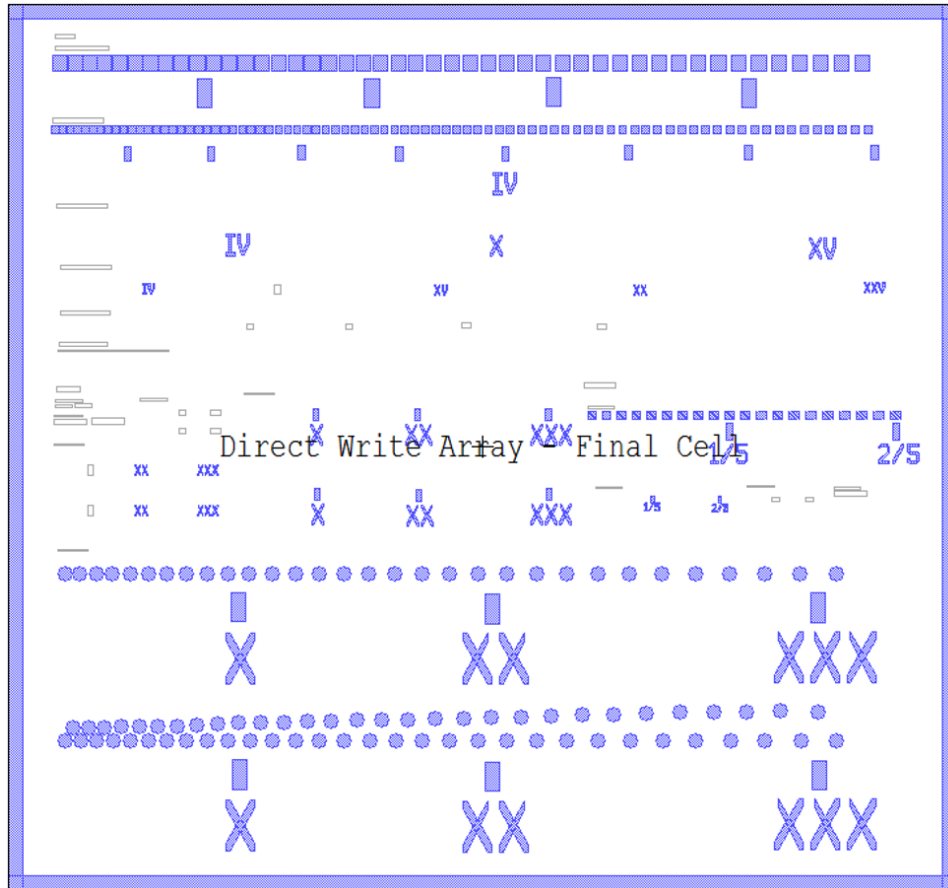


Figure 30: Exposure array design

The three feature shapes used in this study were squares, circles, and triangles. Arrays of alternating triangles at 45° were created to see how resolution varied with angular feature edges. Figure 31 shows a zoomed in image of Figure 30 depicting the smallest square, triangle, and circle arrays in the design.

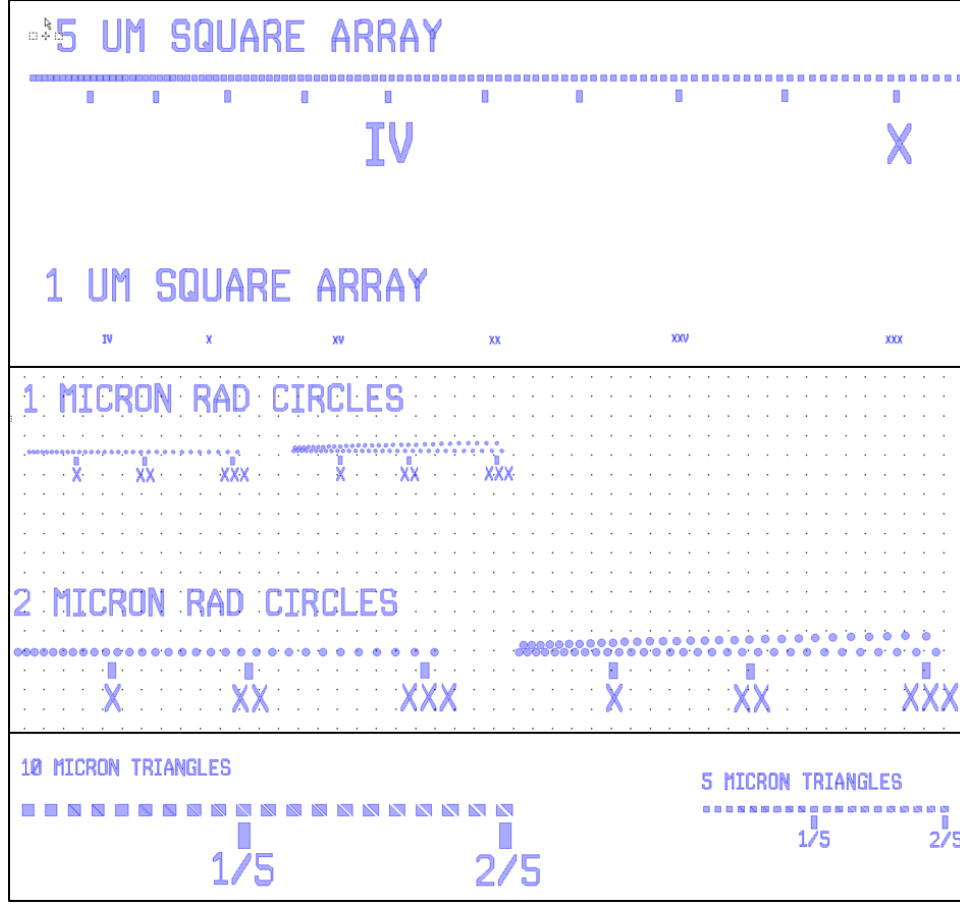


Figure 31: Zoomed in view of the smallest square, circle, and triangle arrays in the exposure design.

Tick marks were used to track feature spacing. Feature dimension's ranged from 1 to 50 μm and the spacing between each feature ranged from 10 nm to 10 μm .

3.5 Approach to Meet Research Objectives

This chapter presented the experimental methodology developed to achieve the desired research goals and introduced the techniques used to analyse the results. To achieve research objectives a 3 parallel research avenues were developed to determine ideal RIE chemistries for selectivity, characterize the anisotropic nature of those chemistries, and develop a method to successfully prepare patterns for etching

on elevated surface. Achieving each avenue will provide the opportunity realize the ultimate ambition of this work.

IV. Results and Analysis

4.1 Anticipated Results

This chapter provides the experimental results of the processes and methodology described in III. The analysis of results is performed and their implications and limitations toward realizing research goals are discussed.

4.2 Selectivity Studies

4.2.1 Initial CF_4/O_2 RIE Selectivity Study

Table 19 shows the arithmetic mean of selectivity of the three replicate units studied for each treatment.

Table 12: Selectivities by gas flow ratio and pressure levels in the initial CF_4/O_2 RIE selectivity study.

	Gas Flow Ratio ($\text{O}_2:\text{CF}_4$)		
Factor A: Pressure	0 (1:10)	1 (1:13)	2 (1:16)
0 (40 mTorr)	0.3359	0.4427	0.4509
1 (50 mTorr)	0.4815	0.4916	0.5344
2 (60 mTorr)	0.6134	0.5965	0.6137

Within the parameters of this study, these results indicate a trend of increasing selectivity as chamber pressure increases and gas flow rate ratio decreases. Initial observation identified chamber pressure as the most important effect on etch selectivity.

A qualitative analysis of factor relationship was performed. Since only two factors were used in this study, each with three levels, each factor could be isolated to determine their relationship to the selectivity of (Si:1818). One factor was held constant

while the other was plotted against selectivity. The levels of the factor held constant were represented by individual data sets. MATLAB was used to generate two plots: selectivity vs. chamber pressure and selectivity vs. gas flow rate ratio. Trend lines were created using the "polyval" and "polyfit" MATLAB commands. Figure 32 shows the data sets and trendlines created.

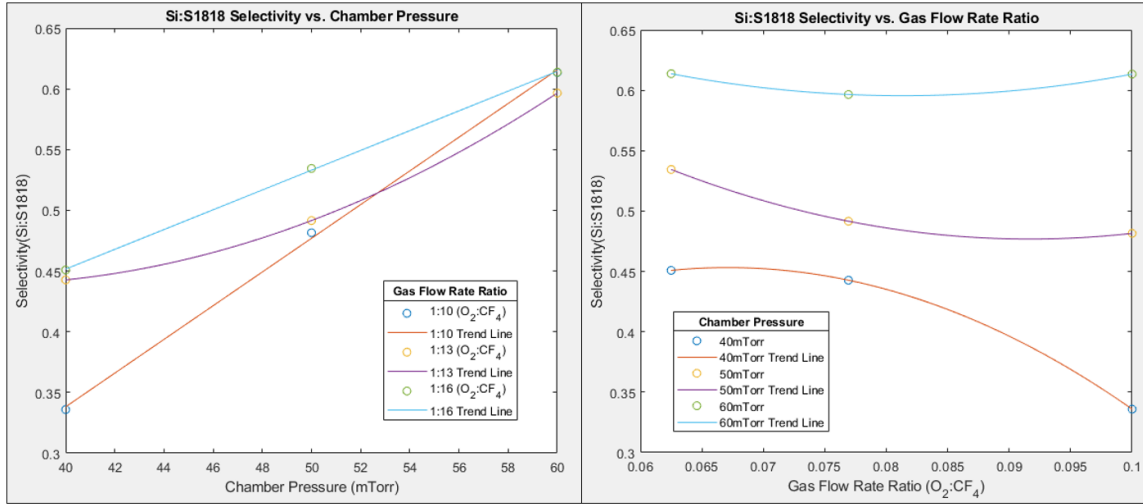


Figure 32: Selectivity trend lines isolating gas flow rate ratio and chamber pressure for the initial CF₄/O₂ RIE selectivity study.

A linear relationship between chamber pressure and selectivity can be clearly seen at the 1:10 and 1:16 (O₂:CF₄) gas flow rate ratio levels. However, there does not appear to be a significantly linear relationship between chamber pressure at the 1:13 (O₂:CF₄). There is no significant linear relationship between gas flow rate ratio (O₂:CF₄) and selectivity at any chamber pressure level. Although there is no conclusive evidence that either chamber pressure or gas flow rate share a linear relationship with Si:S1818 selectivity, visual observation shows that increasing chamber pressure and decreasing gas flow rate ratio seems to improve selectivity. With only three data points each, it is ambitious to assume the trend lines shown in Figure 32 will remain valid through additional chamber pressure and gas flow rate ratios. Therefore, this

analysis of trend lines was left to be qualitative. To better explore factor relationships further analysis was performed.

4.2.1.1 Significance of Factors in the Initial CF₄/O₂ RIE Selectivity Study

ANOVA, regression, and residuals were analyzed to determine factor interactions and relationship to selectivity. Selectivity results modeled as a 3² full factorial were loaded into Minitab along with the corresponding factor information, as shown in Table 13.

Table 13: Factor information for the initial CF₄/O₂ RIE selectivity study.

Factor	Levels	Values
A	3	1, 2, 3
B	3	1, 2, 3

Next, an ANOVA table for the initial CF₄/O₂ RIE selectivity study was generated as shown in Table 14.

Table 14: ANOVA table for the initial CF₄/O₂ RIE selectivity study.

Source	DF	Contribution	Adj SS	Adj MS	F-Value	P-Value
A	2	6.81%	0.014297	0.007148	40.14	0.000
B	2	84.19%	0.176740	0.088370	496.27	0.000
A*B	4	7.47%	0.015679	0.003920	22.01	0.000
Error	18	1.53%	0.003205	0.000178		
Total	26	100%	0.209921			

From Table 14, observance of large F-test values and P-values under an α of 0.05

means the null-hypothesis H_0 can be rejected, thus both chamber pressure and gas flow rate are significant factors for this experiment. Contribution percentages come from the sequential sum of squares which shows how much each component in the ANOVA table varies. The higher the percentage, the more of an effect it has on the overall response.

4.2.1.2 Linear Regression in the Initial CF_4/O_2 RIE Selectivity Study

From Montgomery [10], the recommended linear regression model can be seen in Equation 10.

$$R_1 = \beta_0 + \beta_1 A + \beta_2 B + \beta_{12} AB + \beta_{11} A^2 + \beta_{22} B^2 + \epsilon \quad (10)$$

In addition, the following estimates for each factor, factor interaction, and levels determined as shown in Table 15.

Table 15: Linear regression coefficient estimates and their corresponding high/low 95% confidence intervals using the Gauss-Newton algorithm with 200 max iterations and a tolerance value of 0.00001 in the initial CF_4/O_2 RIE selectivity study.

Parameter	Estimate	SE Estimate	95% CI
β_0	0.141674	0.0487561	(0.0402801, 0.243068)
β_1	0.106461	0.0362797	(0.0310134, 0.181909)
β_2	0.130867	0.0362797	(0.0554190, 0.206314)
β_{12}	-0.028633	0.0059914	(-0.0410931, -0.016174)
β_{11}	-0.005294	0.0084731	(-0.0229152, 0.012326)
β_{22}	0.006356	0.0084731	(-0.0112652, 0.023976)

Since β_{22} and β_{11} contain a zero in their confidence intervals, these effects can be

removed are not significant. Thus, the updated model can be seen in Equation 11.

$$R_1 = 0.141674 + 0.106461 A + 0.130867 B - 0.028633AB \quad (11)$$

Equation 11 can be confirmed with visual observation as the selectivity versus factor plots in Figure 32 show somewhat linear trends.

4.2.1.3 Impact of Factors in the CF_4/O_2 RIE Selectivity Study

This experiment can also be modeled as a Complete Randomized Design (CRD) with nine treatments, each corresponding to a factor setting. This allows us to estimate the contrasts between each setting, and present a box plot for graphical interpretation. MATLAB was used to fit this linear model and find contrast estimates [38]. Confidence intervals are calculated as the t-based two-sided intervals defined by Equation 12 [39]. Of the 36 estimable contrasts, the confidence intervals are clearly centered off of zero in all but five cases. The contrasts between factor settings A2-B2, A3-B3, A3-C3, A2-C2, and B3-C3 contain zero in their confidence interval, and are therefore not statistically significant.

$$\hat{\tau}_i - \hat{\tau}_j = \pm t_{1-\frac{\alpha}{2}}(df_E) \sqrt{\mathbf{c}'\mathbf{c} \times \frac{MSE}{r}} \quad (12)$$

It is interesting to note that all of these insignificant contrasts compare factor settings with the same chamber pressure. This highlights the greater contribution of chamber pressure to the etch selectivity than that from the gas flow ratio. That said, it is important to remember the ANOVA results show the flow ratio is still significant, and that their interaction factor is also important. Hence the benefit of the factorial analysis.

Box and whisker plots provide a five value summary of results and indicates if any

extreme outliers exist. The values generated by box and whisker plots are:

- Minimum
- Maximum
- Median
- First Quartile
- Third Quartile
- Extreme Outliers (Potential 6th Value)

The boxplot of this nine factor CRD, shown in Figure 33 and generated using MATLAB, helps to visualize the trends within each factor, and to some extent, their interaction [40].

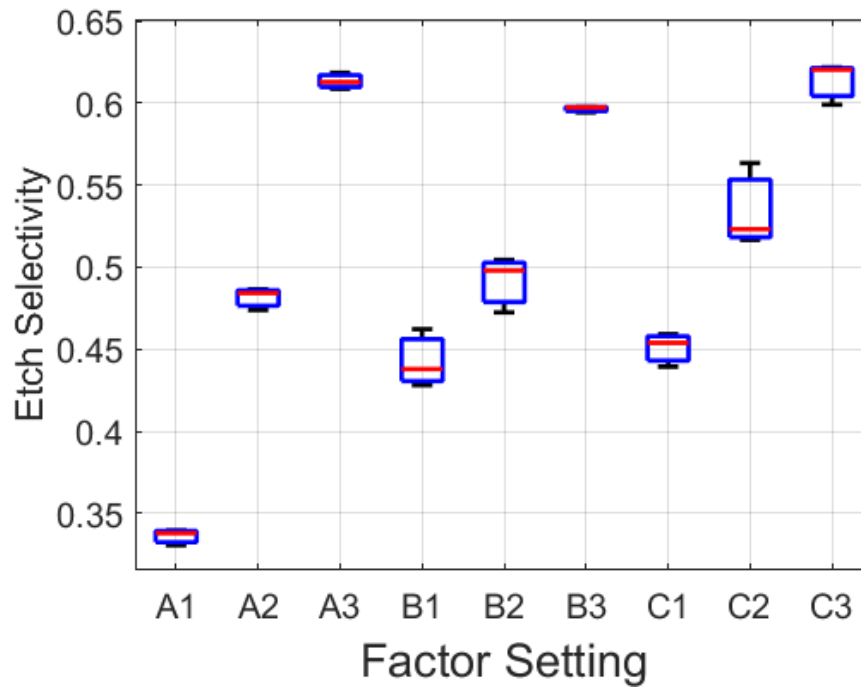


Figure 33: Selectivity boxplots for each factor setting in the initial CF_4/O_2 RIE selectivity study

Interesting results arise when plotting boxplots as a CRD with three treatments by separating the factors and treating their levels as the treatments. These are included in Figure 34 and Figure 35, and were also generated using MATLAB [40]. The stronger influence of the chamber pressure on selectivity can be clearly seen in these graphs, as well as the upward trend from the gas flow ratio. The interaction between the two cannot be easily observed graphically, but is analyzed in the ANOVA table previously discussed.

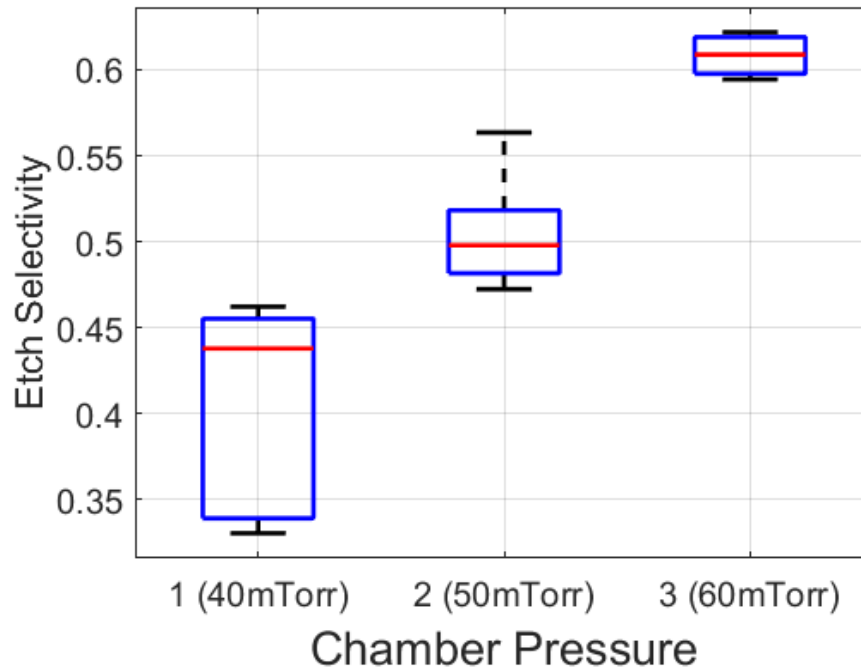


Figure 34: Selectivity by chamber pressure in the initial CF_4/O_2 RIE selectivity study

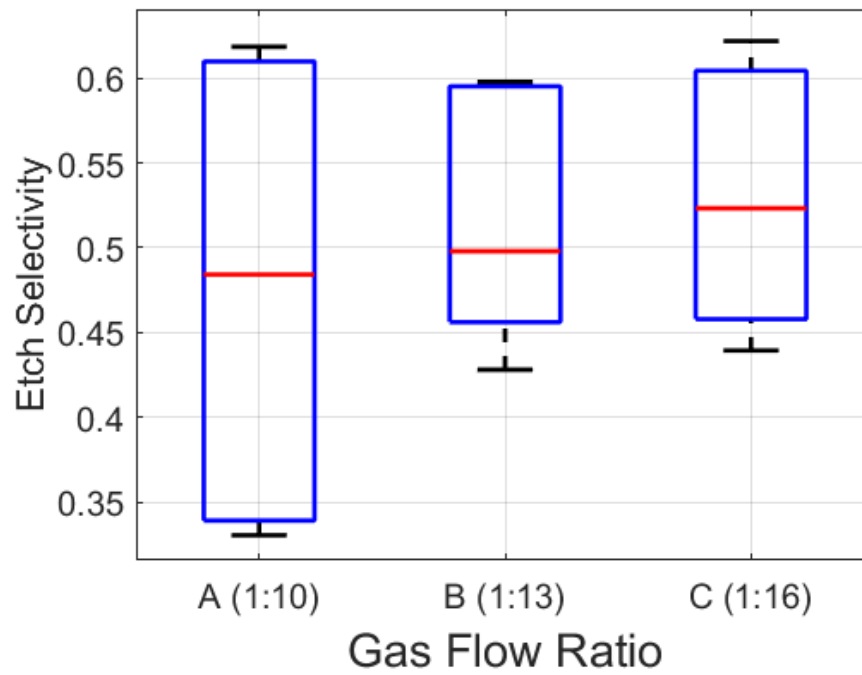


Figure 35: Selectivity by gas flow rate ratio in the initial CF_4/O_2 RIE selectivity study.

Finally, a pareto chart of standardized effects is generated to determine which factors are most critical to etch selectivity [41]. This can be seen in Figure 36.

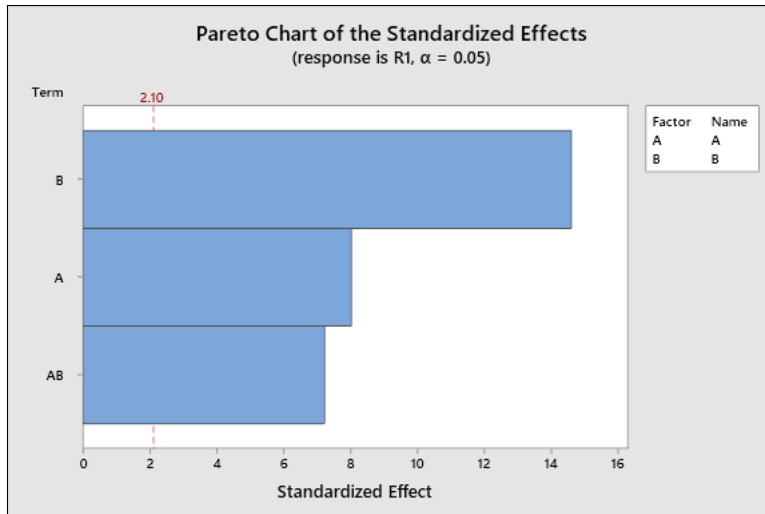


Figure 36: Factor effects of A, B, and AB with critical value at 2.10 in the initial CF_4/O_2 RIE selectivity study

The line at 2.10 represents the critical value for each factor. If the factor is above 2.10, then it is important in the process [41]. It can be seen that both factors A and B, along with their interaction AB, are all in effect when it comes to selectivity.

4.2.1.4 Residuals in the Initial CF_4/O_2 RIE Selectivity Study

Within Minitab, four residual plots have been plotted in Figure 37.

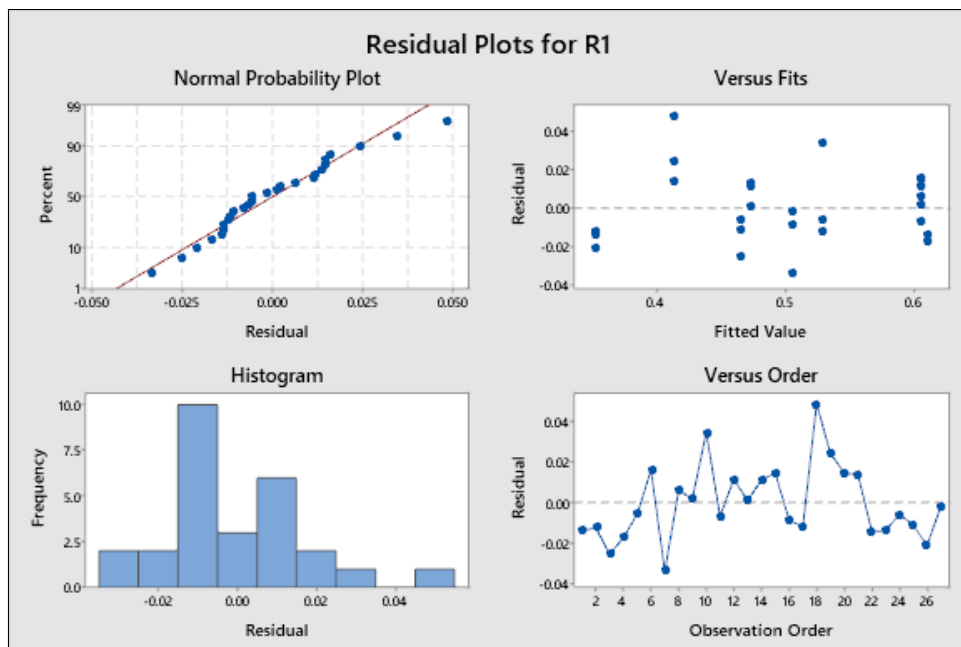


Figure 37: Four plots showing residual comparisons over runs in the initial CF_4/O_2 RIE selectivity study.

From Figure 37, the difference between the actual selectivity value for each run and what the linear regression equation predicts is plotted out using the following: normal probability plot, versus fits plot, histogram plot, and versus order plot. These plots summarize findings and analyze the quality of the experiment.

The normal probability plot shows that all residuals reside along the best-fit line indicating no significant outliers. On the versus fits plot all residuals show a random noise across the center line and their values are grouped fairly close together. The histogram plot indicates a bell curve shape and the versus order plot shows no apparent patterns. Thus, from Figure 37, there are no indications of any problems within the experimental design [42] [43].

4.2.2 Follow-on CF₄/O₂ RIE Selectivity Study

The goal of this study was to use trends determined in the first selectivity and add an additional factor to achieve the determine the chemistry and factor levels providing the highest overall selectivity of silicon (Si) to Photoresist (PR).

This selectivity study used CF₄ and O₂ as the reactive gas species and explored three factors: gas flow rate ratio (CF₄:O₂), chamber pressure, and RF power. Each factor had three levels resulting in a total of 27 different etch treatments. The factor settings for each treatment can be referenced in Table 7 in Section 3.2.3. Table 16 shows the selectivity of Si:PR of each treatment in the second CF₄/O₂ selectivity study.

Table 16: Selectivity of silicon:photoresist of each treatment in the follow-on CF₄/O₂ RIE follow-on selectivity study.

	Factor A: Gas Flow Ratio (O ₂ :CF ₄)								
	0 (1:8)			1 (1:18)			2 (1:28)		
Factor C: Power	0 (70mW)	1 (100mW)	2 (130mW)	0 (70mW)	1 (100mW)	2 (130mW)	0 (70mW)	1 (100mW)	2 (130mW)
Factor B: Pressure									
0 (80mTorr)									
S1818	2.615	2.246	1.586	3.125	1.139	1.117	2.374	1.549	0.859
Bilayer (SF11+S1818)	2.178	1.992	1.645	1.894	1.262	1.168	1.432	1.334	0.793
AZ9260	1.648	1.545	1.634	2.070	0.903	1.128	0.660	1.108	0.770
1(100mTorr)									
S1818	2.361	3.064	1.962	5.001	2.548	1.964	5.929	2.013	1.507
Bilayer (SF11+S1818)	2.899	2.447	1.678	2.472	1.949	1.632	2.030	1.687	1.243
AZ9260	3.197	1.773	1.809	1.786	1.374	1.335	1.684	1.186	1.168
2(120mTorr)									
S1818	9.282	4.183	1.684	5.628	2.397	1.651	4.406	3.597	2.241
Bilayer (SF11+S1818)	3.056	2.630	2.291	2.542	2.234	1.733	2.416	2.192	1.690
AZ9260	2.464	1.779	1.999	1.327	2.141	2.483	1.384	1.486	1.610

Table 16 shows the treatment conditions in the second CF₄/O₂ lead to marked improvement in the selectivity of Si:S1818. Selectivities were then sorted by photoresist and factor. Box and whisker plots for gas flow rate ratio, chamber pressure, and RF power were generated.

Figure 38 shows the box and whisker plots for selectivities sorted by gas flow rate ratio generated in MATLAB [40].

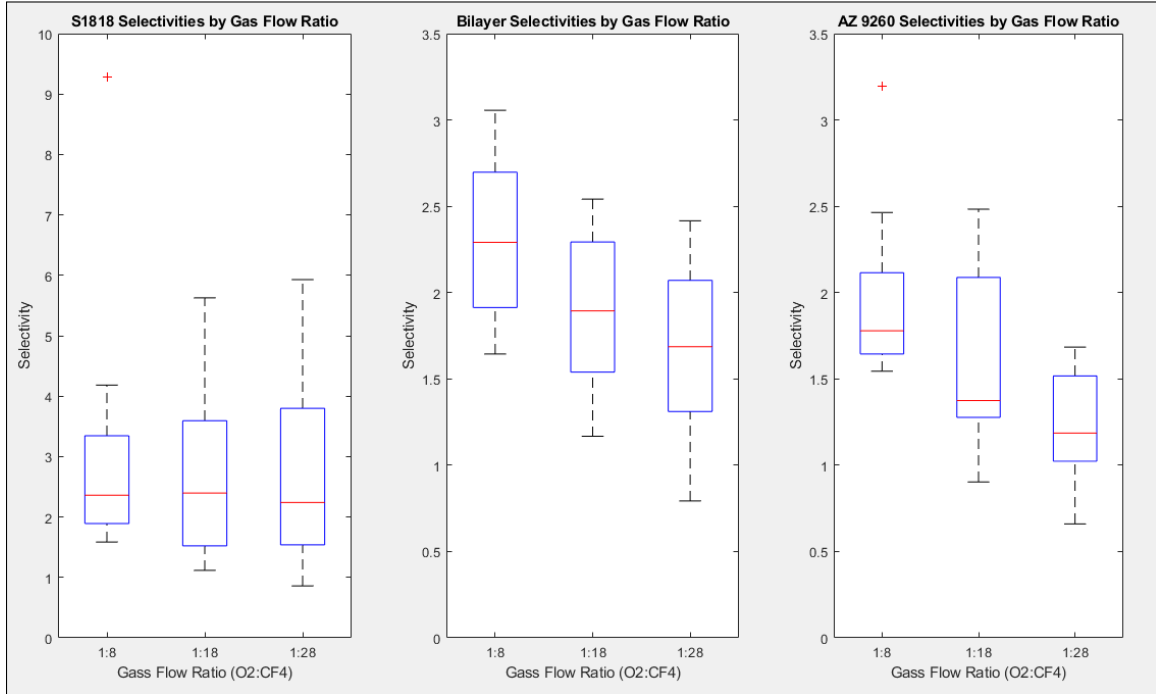


Figure 38: Selectivities by gas flow rate ratio in the follow-on CF₄/O₂ RIE selectivity study.

Initial observation indicates that gas flow rate ratio does not have a significant effect on the selectivity of Si:S1818. There is very little variation between median selectivities. However, as gas flow rate ratio decreases there is an increase in the dispersion and positive skewness of selectivity. There is one extreme outlier with a selectivity of 9.2822:1 (Si:S1818).

Gas flow rate appears to have an effect on both AZ 9260 and the bilayer (S1818+SF-11) photoresists. As gas flow rate increases Si:AZ9260 selectivity decreases. Figure 39 shows etch selectivities sorted by pressure settings.

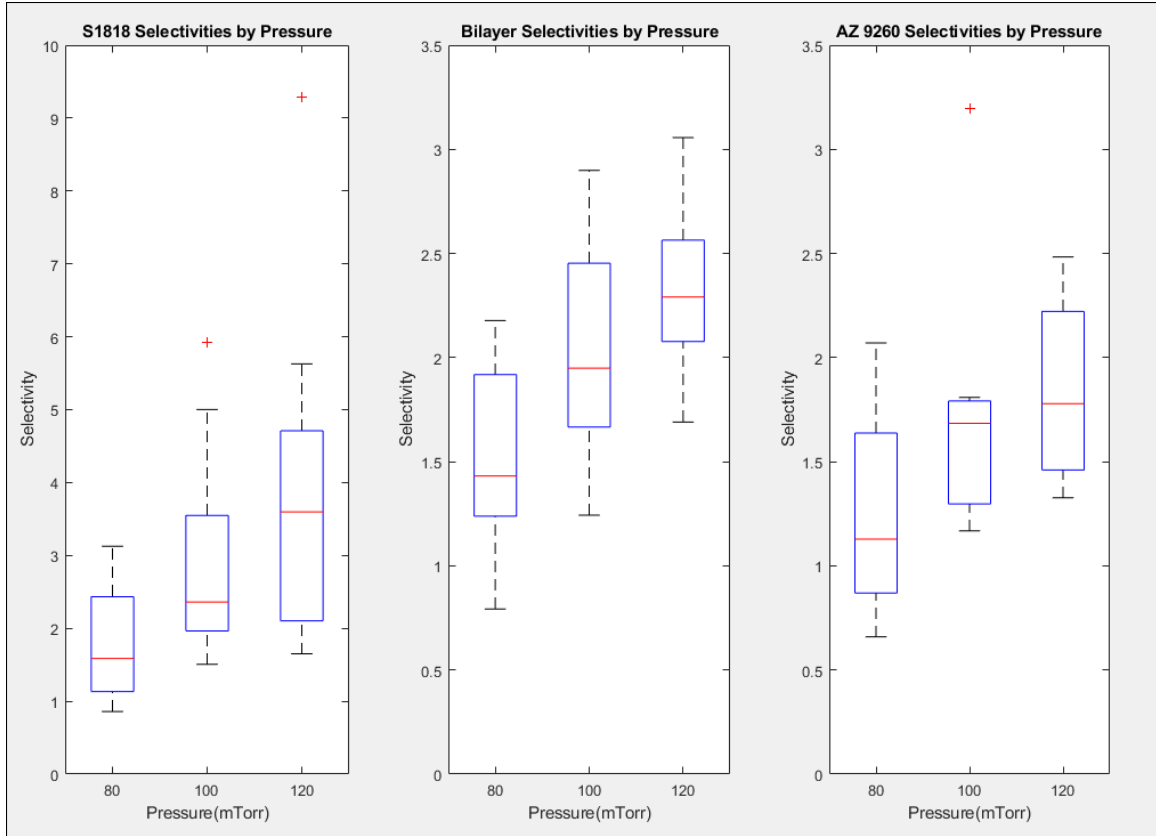


Figure 39: Selectivities by chamber pressure in the follow-on CF_4/O_2 RIE selectivity study.

Initial observation in the selectivity of silicon to S1818 and AZ 9260 photoresists confirms the trend shown in the first study, that increasing chamber pressure improves selectivity. It appears from these results that the pressure limit, where selectivity begins to drop, has still not been reached. There are a few outliers and some skewing toward higher selectivities.

Figure 40 shows etch selectivities sorted by RF power.

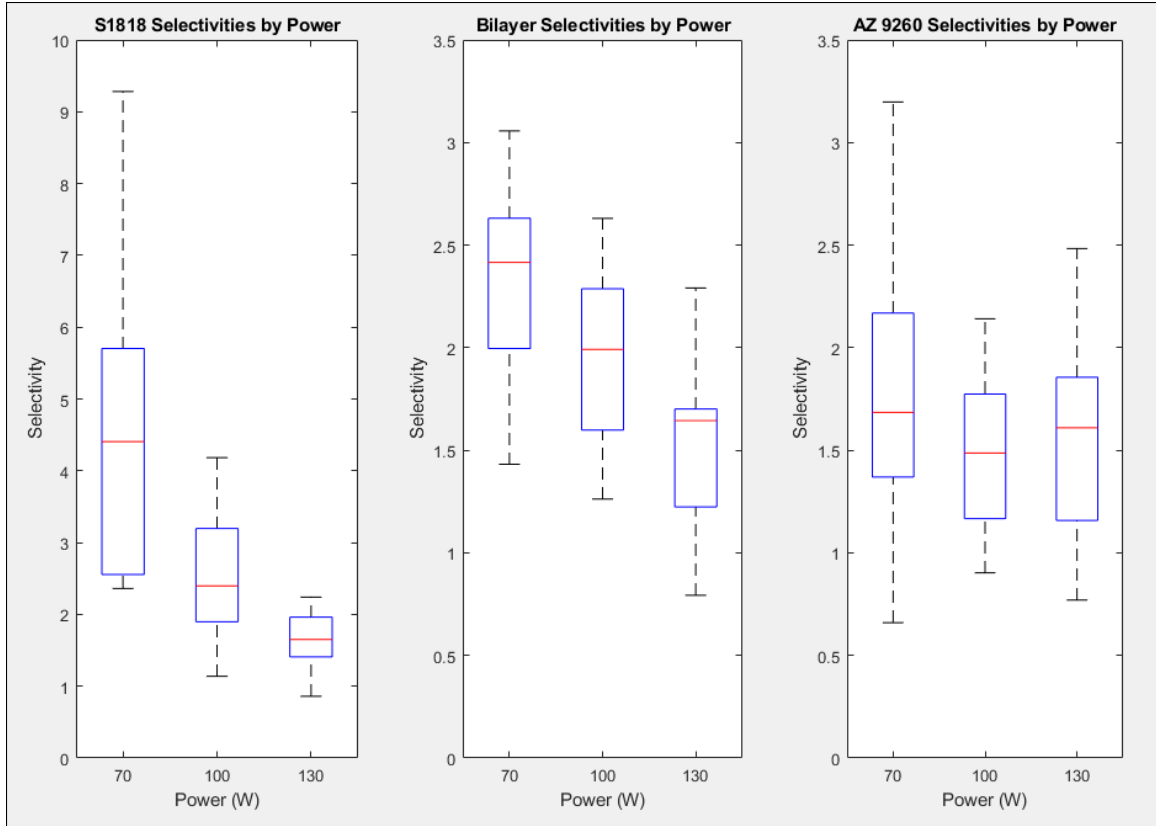


Figure 40: Selectivities by RF Power in the follow-on CF_4/O_2 RIE selectivity study.

Figure 40 indicates that increasing RF power reduces the selectivity of silicon to S1818. RF Power seems to have no significant impact on AZ 9260 selectivity. Bilayer photoresist appears to indicate improved selectivity with increasing RF Power.

From the box and whisker plots the following observations can be made. Gas flow rate ratio appears to have little to no effect on the selectivity of S1818 and bilayer resist, but a significant impact on the selectivity of AZ 9260. As gas flow rate ratio increases, AZ 9260 selectivity decreases.

Chamber pressure appears to have the most significant impact on selectivity of the three factors involved in this experiment. As chamber pressure increases, so do the selectivities of S1818 and AZ 9260, however, the selectivity of the bilayer resist decreases.

RF power appears to have an effect on the S1818 and bilayer resists but no effect on the selectivity of AZ 9260. As RF power increases, S1818 selectivity drops, however, bilayer resist selectivity is improved.

4.2.2.1 Qualitative Analysis of CF_4/O_2 RIE Anisotropy

Attempts were made to characterize the anisotropic behavior of the most selective CF_4/O_2 RIE chemistries determined in the follow-on etch selectivity study. Figure 41 shows an anisotropic analysis of one CF_4/O_2 RIE chemistries.

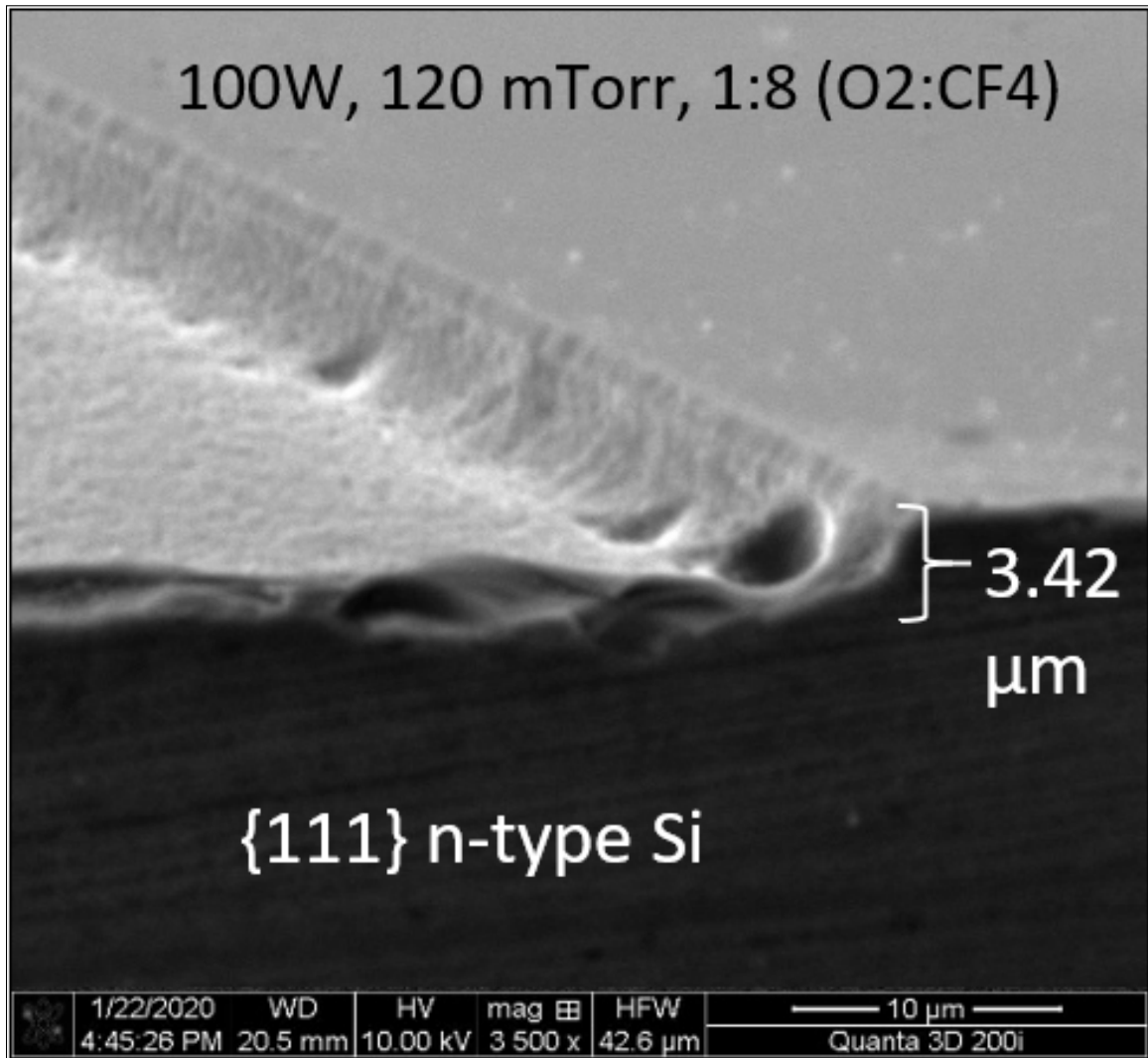


Figure 41: Anisotropy of RIE with CF_4/O_2 on {111} n-type Si.

As aforementioned in 3.2.3.3, analyzing the anisotropic behavior of units from the CF_4/O_2 selectivity studies was extremely challenging, and an additional study could not be performed due to lack of material resources (CF_4). Therefore, additional analysis of the anisotropic behavior of Reactive Ion Etching (RIE) with CF_4/O_2 was not possible.

4.2.3 $\text{SF}_6/\text{CHF}_3/\text{O}_2$ RIE Selectivity Study

This study utilized Direct Write Lithography (DWL) as the PR exposure mechanism and $\text{SF}_6/\text{CHF}_3/\text{O}_2$ as the reactive gas species. A Taguchi fractional factorial design with 4 factors, each with 3 levels, was utilized for a total of 9 treatments. The RIE parameters for each treatment can be referenced in Table 11. Table 17 shows the Si:PR selectivities for the $\text{SF}_6/\text{CHF}_3/\text{O}_2$ RIE selectivity study.

Table 17: Selectivity of silicon:photoresist of each treatment in the $\text{SF}_6/\text{CHF}_3/\text{O}_2$ RIE Selectivity Study.

Treatment	Si:S1818 Selectivity	Si:BiLayer Selectivity	Si:AZ 9260 Selectivity
1	15.562	24.689	2.467
2	20.062	20.263	41.456
3	12.519	14.450	84.586
4	18.532	14.503	21.994
5	2.540	1.886	1.766
6	18.497	16.239	11.783
7	24.720	26.293	18.907
8	10.717	10.192	51.272
9	62.140	24.912	57.168

From Table 17 there are some clear outliers. Notably the selectivity of Si:AZ 9260

in treatment 1 breaks and the selectivity of Si:S1818 in treatment 9. The selectivities of Si:S1818 and Si:Bilayer PR are relatively similar across treatments 2 through 8. The selectivity of Si:AZ 9260 does not follow the same trends seen in S1818 and Bilayer results. In the follow-on CF_4/O_2 selectivity study, the selectivity of Si: AZ 9260 was typically the lowest of the three PRs. In the $\text{SF}_6/\text{CHF}_3/\text{O}_2$ study the opposite seems to be true. This could be due to a number of factors including PR chemical composition and differences due to the utilization of DWL as the exposure mechanism.

The addition of CHF_3 is known to absorb into the photoresist and compete with other radicals without etching [6]. This perhaps indicates that CHF_3 behaves favorably with AZ 9260 and altering its chemistry to delay etching more so than S1818.

The utilization of DWL as the exposure mechanism brought about interesting observations in the development of AZ 9260. In the CF_4/O_2 follow-on selectivity study, a flood exposure was performed on AZ 9260 using a 850 mJ/cm^2 dose of 365 nm i-line radiation and developed with AZ 726 MIF developer. However, DWL exposures on AZ 9260 using AZ 726 MIF developer failed to properly develop features. Initially, considering AZ 726 MIF developer had been effective at developing AZ 9260 after flood exposures, the prevailing theory was that DWL was not providing enough energy to develop features. However, after performing a full-spectrum DWL exposure optimization study, it was observed that AZ 726 MIF developer was unable to properly develop the exposed features no matter the DWL exposure dose applied. Figure 42 shows the results of one batch exposure on AZ 9260 with varying exposure doses performed with the Heidelberg μPG101 Micro Pattern Generator.

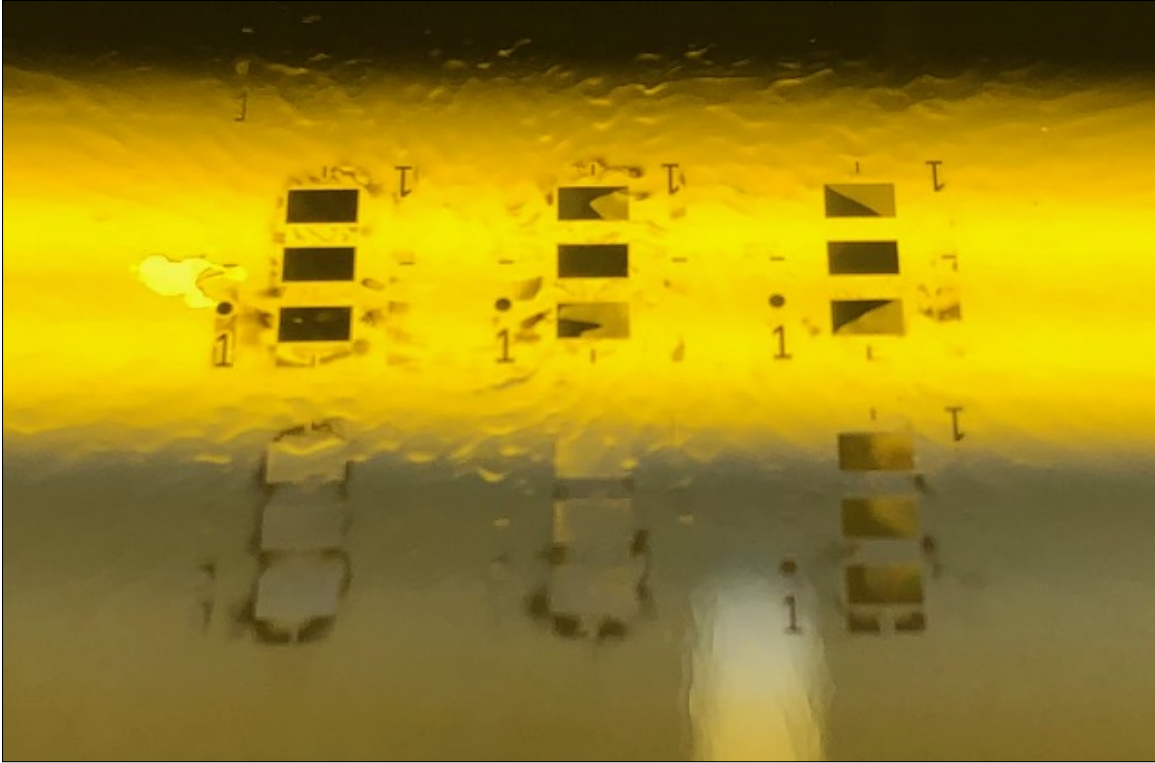


Figure 42: Batch DWL exposure performed on AZ 9260 with varying exposure doses after 14 minute development in AZ 726 MIF developer.

In the top row especially, there is indication that high power DWL exposures damage the photoresist in such a way that it can not be developed. The mechanisms causing these observations are not fully understood and should be explored in future work. Additional background research indicated that 351B may be a suitable alternative to AZ 726 MIF developer. After performing an additional DWL exposure optimization study it was found that an exposure power (20 mW), a pulse duration of 40-90% and stage speed of 1x1, features were successfully developed in AZ 9260 using 351B developer.

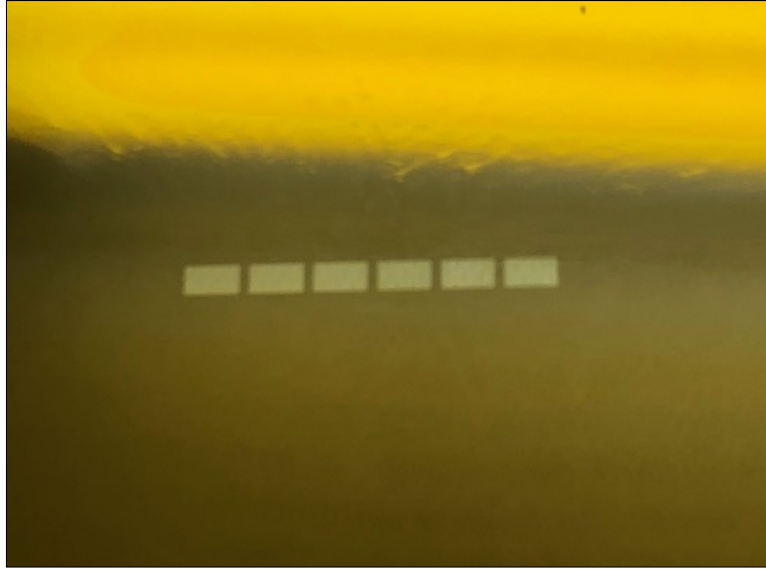


Figure 43: Batch DWL exposure performed on AZ 9260 at 20 mW, 40-90% pulse duration, and 1x1 stage speed after 2 minute development in 351B developer.

After development features appeared well defined when analyzing results using a microscope. Two additional observations worth noting arose from the DWL exposure of AZ 9260. The appearance of distinct surface alteration over any regions the beam had passed over but not exposed and a seemingly tapered feature sidewall. Figure 44 shows the surface alterations in regions the beam passed over but did not expose.

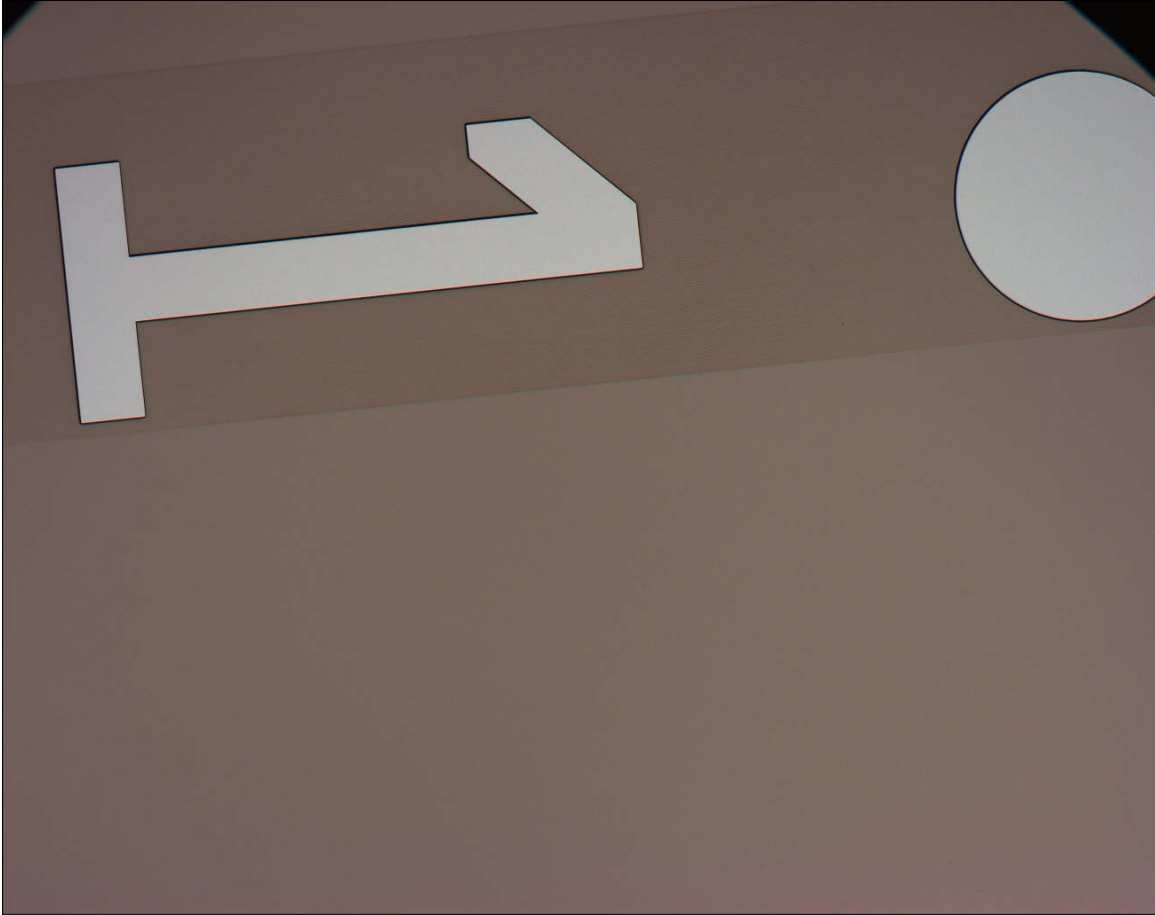


Figure 44: Microscope image of DWL performed on AZ 9260 after development.

Note the distinct color difference in regions of unexposed photoresist around exposed features. This discoloration appeared only on AZ 9260 units exposed using DWL and developed with 351B developer. Figure 45 again shows the surface alterations in regions the beam passed over but did not expose, this time after a RIE treatment was performed.

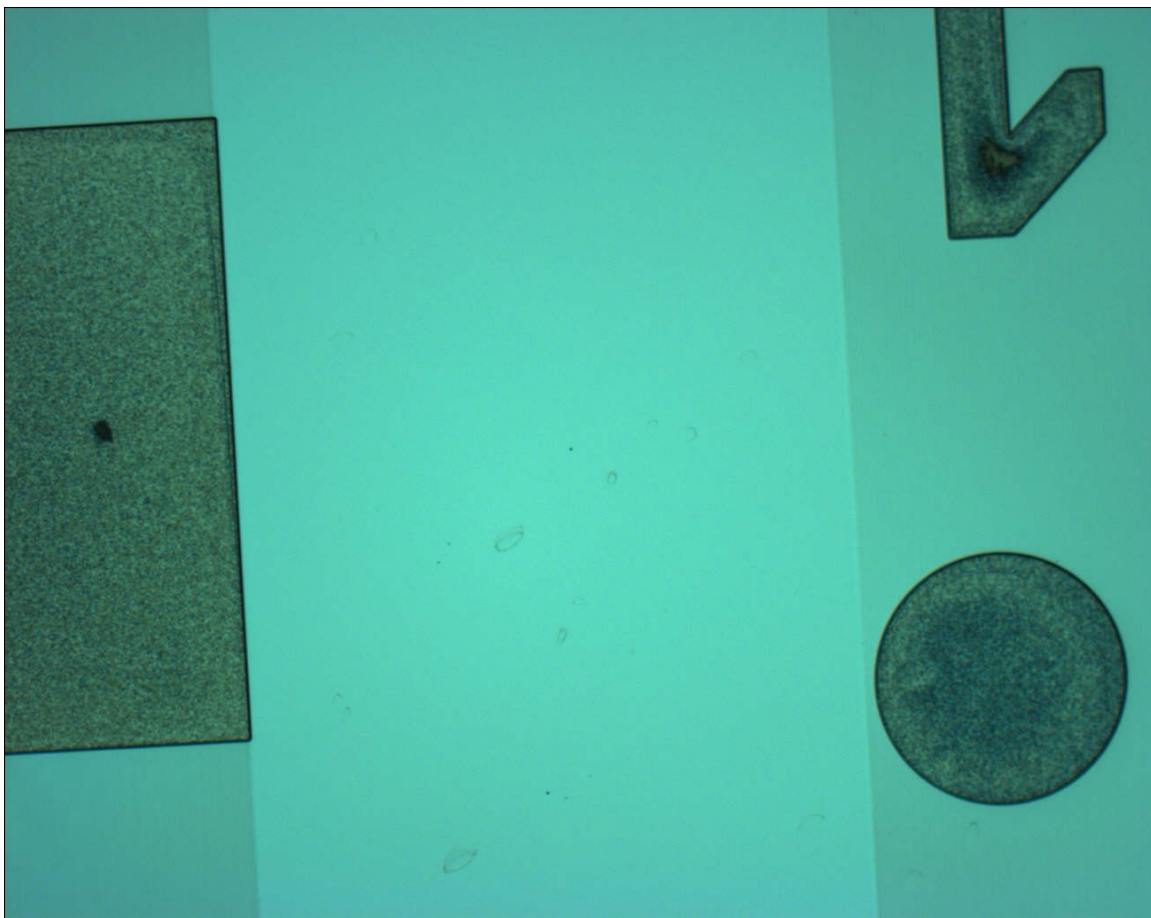


Figure 45: Microscope image of DWL performed on AZ 9260 after applying an RIE treatment.

Although Figure 45 was taken following an RIE treatment, these lines were clear from visual observation after development and appeared in parallel with any exposed features. It is likely that the imaging objective used to focus and align the beam in the Heidelberg μ PG101 Micro Pattern Generator is unintentionally producing a form of Electromagnetic (EM) exposure at a wavelength the Photoactive Compound (PAC) in AZ 9260 can absorb. Additionally, although features appeared well defined after development, as indicated in Figure 44, profilometer measurements taken to determine the initial PR thickness indicated a tapering at the edge of the AZ 9260 features. Figure 46 shows the difference between a typical profilometer measurement

and those taken on AZ 9260 units after DWL exposure and development in 351B.

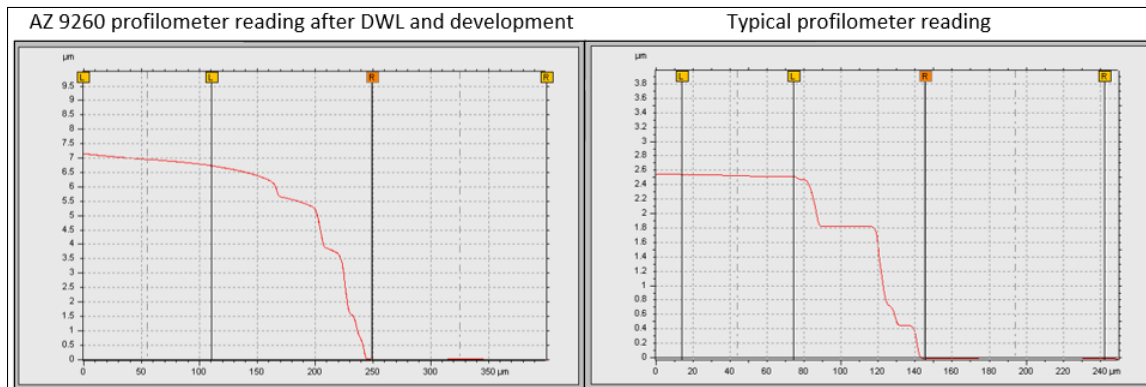


Figure 46: Comparison of a typical profilometer reading on PRs (right) and a profilometer reading on AZ 9260 after DWL and development using 351B.

The slope profile between the top and bottom of features is attributed to noise generated as the profilometer makes a major shift in step height. The primary area of concern is in the difference in slope profiles at the highest regions (left side) of the measured features. While typical profilometer measurements were mostly level at the top of PR features, those taken on AZ 9260 units were clearly tapered. This is likely attributed a combination of overexposure and over development.

These observations did not present when performing DWL on S1818 PR. However, they should be taken into account in future work and considered when performing DWL on thick, high resolution PRs similar in chemical composition to AZ 9260.

Despite issues arising when performing DWL on AZ 9260 this study provided important results to achieving the overall research objective. Ultimately, it showed that RIE with $\text{SF}_6/\text{CHF}_3/\text{O}_2$ produces a much more selective etch and faster Si etch rate than CF_4/O_2 . A summary all three selectivity studies performed in this work can be found in Appendix A.

4.3 Qualitative Analysis of $\text{SF}_6/\text{CHF}_3/\text{O}_2$ RIE Anisotropy using DWL

Once the $\text{SF}_6/\text{CHF}_3/\text{O}_2$ RIE selectivity was performed, the anisotropy of the deepest etches were performed. Features were filled with adhesive to protect the profile then diced. Two different RIE treatments with $\text{SF}_6/\text{CHF}_3/\text{O}_2$ as the reactive gas were characterized. The anisotropic etch behavior between treatments and S1818, Bilayer, and AZ 9260 PR masks were observed. Note that a tilt in some images is due to the orientation of the unit during imaging, not the etch characteristics. In some cases, the best image of anisotropy was obtained by rotating the unit slightly off-axis. Figure 47 shows the results of performing RIE treatment 4 from the $\text{SF}_6/\text{CHF}_3/\text{O}_2$ selectivity study on units masked with S1818, Bilayer, and AZ 9260 PR.

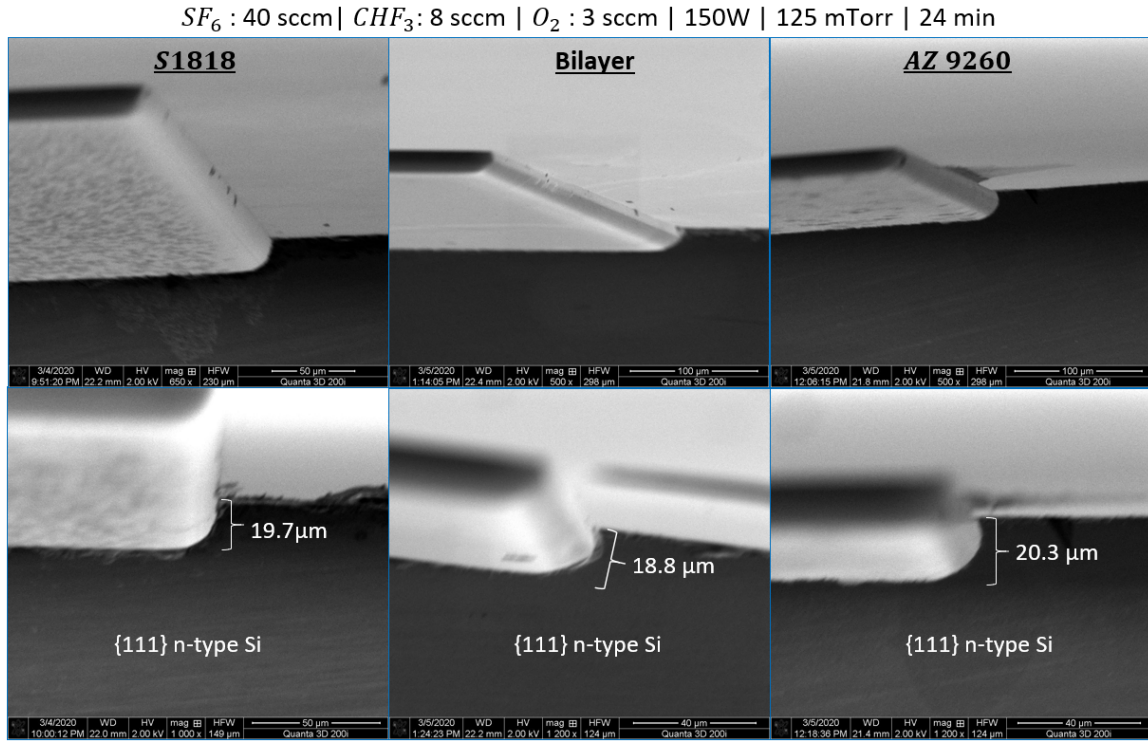


Figure 47: SEM images for anisotropic etch characterization of RIE treatment 4 from the $\text{SF}_6/\text{CHF}_3/\text{O}_2$ selectivity study on units masked with S1818, Bilayer, and AZ 9260 PR.

From Figure 47 there appears to be some surface transformations on the S1818 and AZ 9260 units while the Bilayer surface appears smooth and uniform. There is indication of some isotropic behavior. Although the etch depths are relatively similar, it appears that as the thickness of PR increases, from S1818 (1.9 μm) to Bilayer (3.35 μm) to AZ 9260 (11 μm), there is a greater degree of isotropy.

Figure 48 shows the results of performing RIE treatment 8 from the $\text{SF}_6/\text{CHF}_3/\text{O}_2$ selectivity study on units masked with S1818, Bilayer, and AZ 9260 PR.

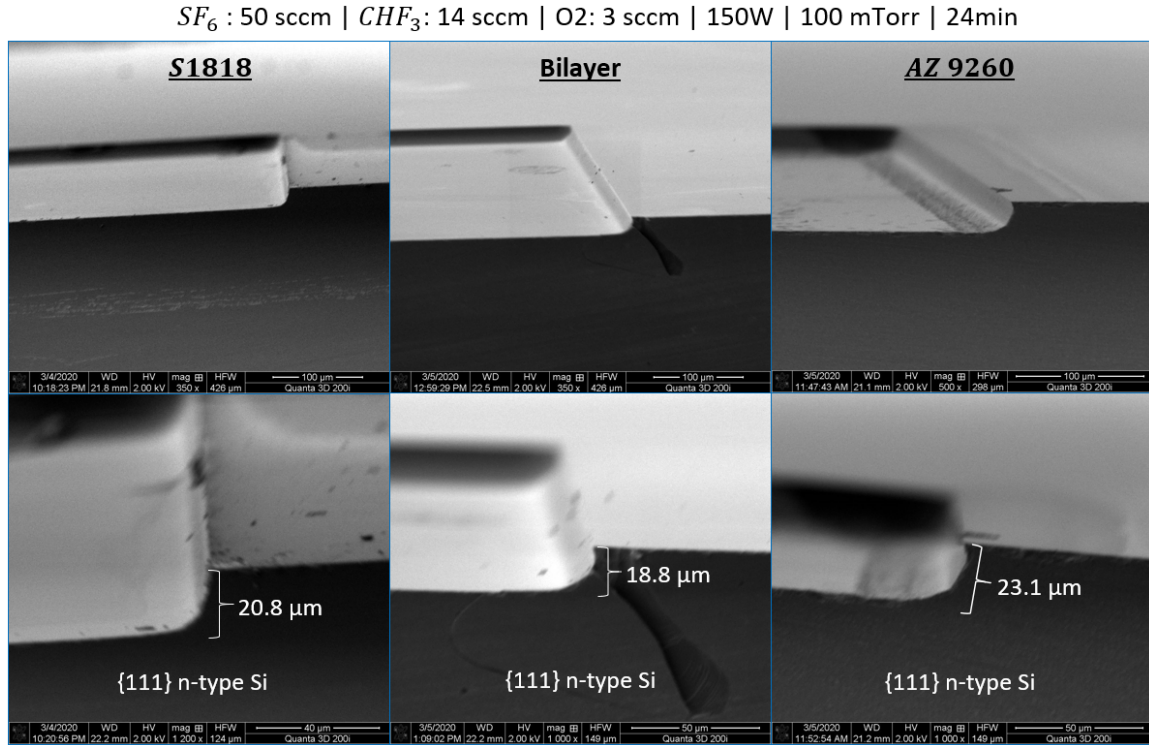


Figure 48: Anisotropic etch characterization of $\text{SF}_6/\text{CHF}_3/\text{O}_2$ treatment 8.

In this case, there appears to be some surface defects on each unit, likely due to damage or residue from etching. Additionally there appears to be a major surface transformation at the bottom of the AZ 9260 trench feature. Again, observation shows that increasing PR thickness results in a greater degree of isotropy. This trend found in both RIE treatment chemistries is likely due to differences in sidewall passivation.

The difficulty in formation of passivation species at the bottom of deeper trenches allows lateral etching to be more prevalent.

Finally, a test was performed reach a maximum etch depth and characterize the anisotropic behavior of RIE with $\text{SF}_6/\text{CHF}_3/\text{O}_2$. Treatment 8, the same used in Figure 48, was performed on a unit masked with AZ 9260 for 1 hr 15 min. Figure 49 shows the result of this experiment.

SF_6 : 50 sccm | CHF_3 : 14 sccm | O_2 : 3 sccm
150W | 100 mTorr | 1hr 15min

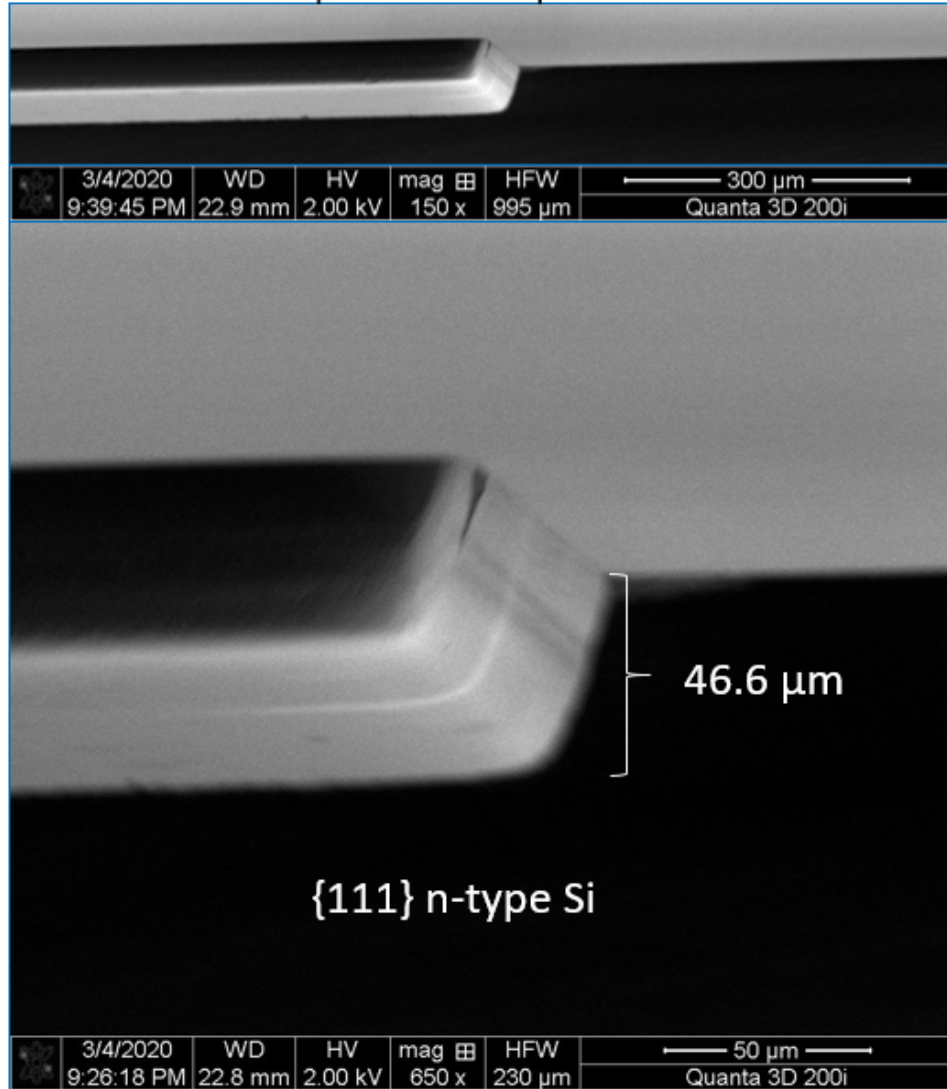


Figure 49: Deep 46.8 μm anisotropic etch characterization of $SF_6/CHF_3/O_2$ treatment 8.

After etching there was still approximately 3 μm of PR remaining on the surface, showing that there is still opportunity to etch deeper. From Figure 49 there is no indication of isotropic behavior. In fact, this profile is more characteristic of a highly physical etch process. Section 4.2.3 identified tapering in the AZ 9260 masked units.

As etching continued, this tapering in the PR likely became more prominent and manifested itself in the Si etch profile. This result provided validation that a deep, selective, anisotropic etch could be achieved using standard RIE.

4.4 DWL for RIE on Elevated Rectangular Substrates

The ability of the Heidelberg μ PG101 to perform DWL on a 2000 μ m elevated, non-circular surface was verified. Figure 50 shows the result of DWL on a 3 stack elevated wafer masked with a 10 μ m layer of AZ 9260 PR.

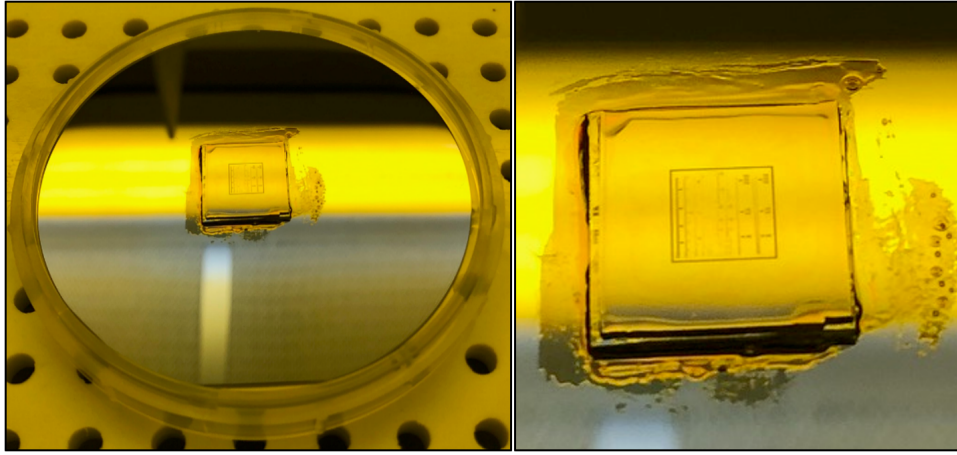


Figure 50: Direct Write Laser Exposure Design on 2000 μ m high elevated wafer masked with 10 μ m of AZ 9260.

There is clear evidence of edge beading due to the rectangular geometry of the substrate as described in Section 2.2.3. However, the center of the diced wafer appears uniform. The Heidelberg μ pg101 was able to successfully find the center of the wafer and expose the desired design on the surface. Optimal exposure settings had not yet been determined and this exposure was done at 25 mW, 1x4 exposure setting, and 90% pulse duration. Figure 51 shows a zoomed in portion of this exposure design.

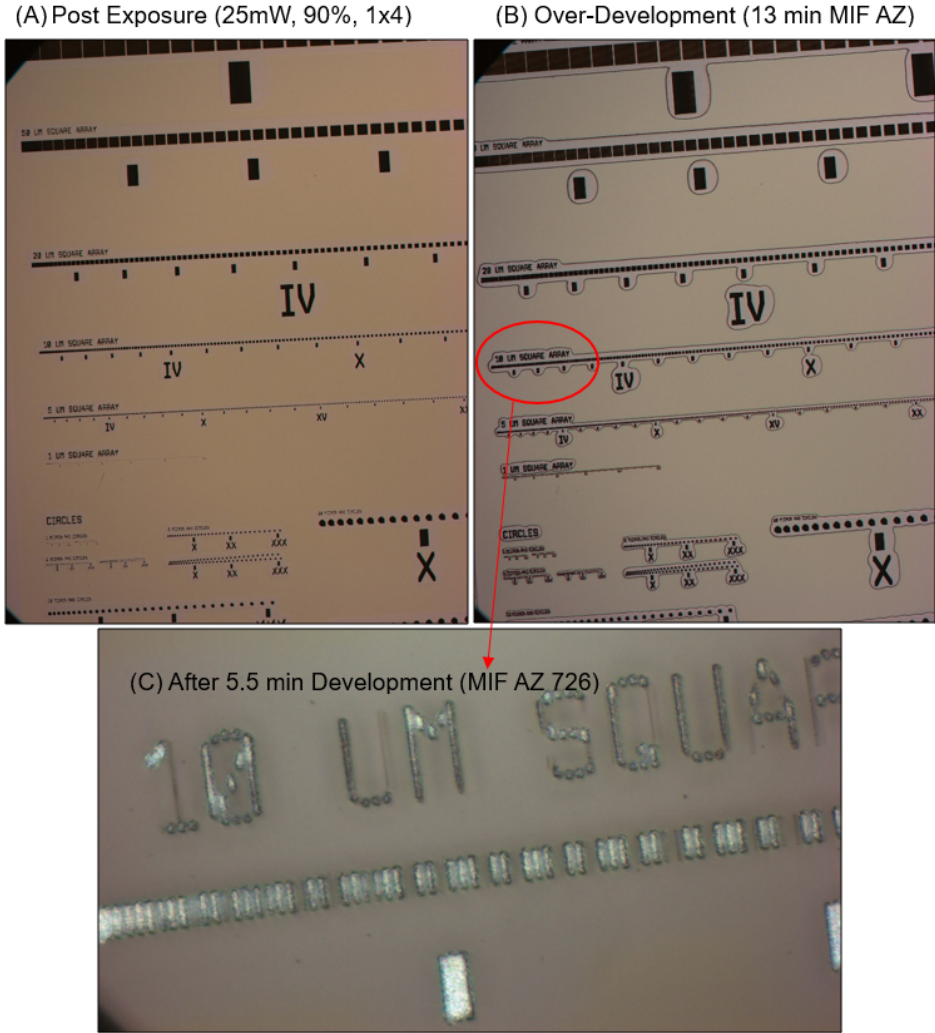


Figure 51: Direct Write Laser Exposure 10 μm square array on 3 Stack Elevated Wafer Coated with 10 μm AZ 9260. (A) Post Exposure. (B) Overdevelopment after 13 minutes in AZ MIF 726 developer. (C) 10 μm square array after 5.5 minutes of development in AZ MIF 726.

In Figure 51, image (A) shows the design array after exposure but before development. Initial observation appears to show a successful exposure. However, after development in AZ 726 MIF developer shows that these exposure settings and subsequent development was unsuccessful. Image (B) shows the same location after 13 minutes in AZ 726 MIF developer. Image (B) shows the 10 μm square array after 5.5

minutes in AZ 726 MIF developer. Future work should determine the optimal DWL exposure settings and developer for high resolution features AZ 9260.

4.5 Meaningful Results and Analysis

The first CF_4/O_2 selectivity study identified that both factors, chamber pressure and gas flow rate, are significant factors but chamber pressure has a more significant impact on selectivity. Linear regression showed that a somewhat linear relationship exists between both factors and selectivity and again highlighted chamber pressure as the more significant factor. The residuals plots did not indicate any problems with experimental design. The selectivity Trends and methodology in the first selectivity study were used to develop the second CF_4/O_2 selectivity study.

The second CF_4/O_2 selectivity study identified ideal selectivity chemistries for achieving high selectivity of Si to three different photoresists with varying thicknesses. Treatment conditions led to marked improvements in selectivity over those in the first. This shows that at low pressures, selectivity is significantly reduced. Trends found in the first selectivity study were confirmed to carry through the second. Also there seems to be a clear relationship between photoresist thickness and selectivity.

The third selectivity study observed $\text{SF}_6/\text{CHF}_3/\text{O}_2$ as the reactive gas species under varying RIE chamber factor settings. This study showed that $\text{SF}_6/\text{CHF}_3/\text{O}_2$ has a much greater selectivity of Si:PR and Si etch rate than CF_4/O_2 .

The anisotropic behavior of RIE chemistries using $\text{SF}_6/\text{CHF}_3/\text{O}_2$ as a reactive gas species was explored. Between two $\text{SF}_6/\text{CHF}_3/\text{O}_2$ chemistries, it appeared that with increasing PR thickness there was an increase in the isotropy of the etch. Future work should look to observe if this trend holds true through additional RIE $\text{SF}_6/\text{CHF}_3/\text{O}_2$ chemistries and applies to other reactive gas species such as CF_4/O_2 .

The potential for DWL to produce high resolution features on an elevated rectan-

gular substrate was confirmed. However, optimal exposure and development settings must be explored in future work.

V. Conclusions

5.1 Revisiting Research Objectives

The methodology and analysis for this work focused on determining the viability of using Direct Write Lithography (DWL) to overcome challenges post by traditional photolithography for the Reactive Ion Etching (RIE) of silicon (Si) and additional materials microelectronics and Microelectromechanical Systems (MEMS) development and modification. The ability of DWL to produce high resolution features on elevated rectangular substrate surfaces was explored.

5.2 Selectivity Studies

5.2.1 Initial CF_4/O_2 RIE Selectivity Study

This experiment showed a strong correlation between the chamber pressure of the RIE system and the etch selectivity between silicon and photoresist, encompassing 84.19% of the sequential sum of squares (most effect on the selectivity response), compared to only 1.53% of the sequential originating from random error. The gas flow ratio also has a less profound, but still statistically significant effect, contributing 6.81% to the sequential sum of squares. The interaction between these factors is also significant and should not be ignored, actually contributing more to the sum of squares than the gas flow ratio at 7.47%. Special care should be taken to optimize the chamber pressure due to its large effect. A regression model fit to the data provides a reasonable estimate of etch selectivity in these factor regimes, based on clearly off axis confidence intervals and properly distributed residual plots. The contrasts and variance of the individual factor settings are plotted for visual interpretation in a boxplot. Finally, a linear relationship between chamber pressure and selectivity was confirmed.

The highest selectivity of 0.6204:1 in silicon vs. photoresist was obtained using the highest pressure (60mTorr) and highest gas flow rate ratio (O_2 - 3 SCCM, CF_4 - 48 SCCM). While even higher selectivity was desired, as the protective photoresist is still etched faster than the silicon, this formed a starting point for future characterization of RIE chemistry selectivity.

5.2.2 Follow-on CF_4/O_2 RIE Selectivity Study

This selectivity study built upon the first and confirmed the trend found regarding chamber pressure but interesting observations regarding gas flow rate ratio. Increasing chamber pressure appeared to result in increasing selectivity for all Photoresists (PRs). Theoretically, there should be a point where chamber pressure is high enough to impact the mean free path of reactive gas species and reduce etch rates but that point that point has not yet been determined. A chamber pressure of 120 mTorr appears to provide the best selectivity of the pressures observed in this study. Increasing gas flow rate ratio ($O_2:CF_4$) appeared to have a detrimental effect on the selectivity of the Bilayer and AZ 9260 PRs but a less prominent affect on S1818. This trend seems to indicate that O_2 has a generally greater impact on the Si etch reaction than the etching of PR at a flow rate of 3 sccm. Increasing RF power appeared to have negative impact on the selectivity of S1818 but less of an impact on AZ 9260 photoresist. However, reducing RF power also reduces Si etch rate. Great improvements in selectivity were made over the initial CF_4/O_2 selectivity study with a maximum of 9.282. Future work should look to pursue these trends to determine a maximum selectivity for RIE with CF_4/O_2 .

5.2.3 SF₆/CHF₃/O₂ RIE Selectivity Study

This study showed that SF₆/CHF₃/O₂ has a much greater selectivity of Si:PR and Si etch rate than CF₄/O₂. Performing DWL on S1818 was relatively straight forward. Performing DWL on AZ 9260 brought observations and challenges which should be explored further. Although a flood exposure using a 850 mJ/cm² dose of 365 nm i-line radiation and developed with AZ 726 MIF developer successfully developed features in AZ 9260 in the CF₄/O₂ follow-on selectivity study, DWL exposures on AZ 9260 using the AZ 726 MIF developer failed to properly develop features. There appeared to be clear evidence that the directed energy beam of the Heidelberg μ PG101 Micro Pattern Generator can severely damage the AZ 9260 PR. The energy was stepped down and the use of 351B developer allowed for the development of features in AZ 9260 using DWL. Performing RIE using SF₆/CHF₃/O₂ as the reactive gas species under the experimental parameters resulted in average selectivities of 20.5876 for S1818 PR, 17.0475 for Bilayer PR, and 32.3778 for AZ9260.

5.3 Qualitative Analysis of SF₆/CHF₃/O₂ RIE Anisotropy using DWL

Seven units between two RIE chemistries using SF₆/CHF₃/O₂ as the reactive gas were studied. The average etch depth among all three PRs between two RIE treatments was approximately 20.25 μ m. Etch isotropy appeared to increase with increasing PR thickness, likely a due to the inhibition of sidewall passivation. A 46.6 μ m etch was performed and indicated no isotropy but instead showed a slight slope inward. This could likely be attributed to tapering transferred from the AZ 9260 PR into the final etch profile. Clearly, SF₆/CHF₃/O₂ is the superior reactive gas species over CF₄/O₂ for deep, selective, anisotropic RIE of Si.

5.4 DWL for RIE on Elevated Rectangular Substrates

The capability of using DWL for RIE on elevated rectangular surfaces was confirmed. DWL has the ability to overcome problems posed by edge beading, geometric, and Bernoulli effects that arise when spin-coating rectangular substrates. Future studies should explore the optimal exposure and development settings for DWL using the Heidelberg μ PG101 Micro Pattern Generator.

5.5 Future Work

This work established the groundwork and techniques required for performing highly selective RIE using DWL. A number of opportunities are available for future exploration and listed below.

- Explore the use of SU-8 photoresist as a mask for Silicon. SU-8 has ideal structural characteristics for vertical sidewalls in thick films, is capable of absorbing wavelengths above 360 nm, and can produce high aspect ratio structures. [44].
- Explore additional high resolution photoresists. Consumer demands for increased functionality and reduced size in the microelectronics and MEMS field has driven the development of advanced photoresists which provide higher resolutions and greater aspect ratios [44]. Further exploration can be performed on the impact of aspect ratio on etch selectivity and the ultimate feature resolution this process can yield.
- There is opportunity to study how spin speed parameters, different cycles, and processing can reduce edge beading, geometric, and bernoulli effects when spinning photoresist onto rectangular substrates. [3] [2]. Additionally, the effect of photoresist hardbake times and temperatures after development on the sidewall profile of features, etch selectivity, and anisotropy of RIE can be studied. [13].

- For increased selectivity, processes to create an aluminum mask can be explored. Photoresist can be applied to the surface, patterned and developed, then aluminum deposited for lift off. Remove unwanted photoresist and perform RIE. Aluminum has exceptionally high selectivity in fluorine-based RIE processes [17].
- Based on observations within this work regarding DWL on AZ 9260, proximity effects, and light distribution in the focal spot for DWL with the Heidelberg μ PG101 Micro Pattern Generator should be explored [14].
- RIE can be performed at low temperatures (cryogenic or helium cooled chamber) to improve selectivity and anisotropy. Also, alternative etching techniques such as ICP and IBE offer great opportunity for achieving deep etch profiles in materials other than Si.

5.6 Success in Achieving Research Objectives and Identified Opportunities

This work established DWL as a viable alternative to traditional photolithography for patterning features on elevated rectangular substrates. The selectivities of two reactive gasses for Si to three different PRs under various RIE factors and levels were studied. $\text{SF}_6/\text{CHF}_3/\text{O}_2$ Using a $10\text{ }\mu\text{m}$ mask layer of AZ 9260 PR a $46.6\text{ }\mu$ anisotropic etch was achieved in Si using standard RIE. This thesis provided the groundwork and proof of concept for a process that yields great potential if refined and developed in future studies.

Appendix A. Tabulated Values for All Selectivity Studies

Table 18: Tabulated values for all RIE selectivity studies including Si:PR selectivity and Si etch rate.

Treatment	Wafer Characteristics			Reactive Gas #1		Reactive Gas #2		Reactive Gas #3		RIE Chamber Settings			S1818 (~1.9µm)		Bilayer (SF11+S1818) (~3.35µm)		AZ 9260 (~11.4µm)	
	Orientation	Doping	Feature Area (µm) ²	Species	Flow Rate (sccm)	Species	Flow Rate (sccm)	Species	Flow Rate (sccm)	Pressure (mTorr)	RF Power (W)	Etch Time (Sec)	Si:PR Selectivity	Si Etch Rate (nm/min)	Si:PR Selectivity	Si Etch Rate (nm/min)	Si:PR Selectivity	Si Etch Rate (nm/min)
Screening CF4/O2 RIE Selectivity Study																		
1	100	n-type	160,000	CF4	30	-	-	O2	3	40	100	600	0.336	43	-	-	-	-
2	100	n-type	160,000	CF4	30	-	-	O2	3	50	100	600	0.482	71	-	-	-	-
3	100	n-type	160,000	CF4	30	-	-	O2	3	60	100	600	0.613	91	-	-	-	-
4	100	n-type	160,000	CF4	39	-	-	O2	3	40	100	600	0.443	57	-	-	-	-
5	100	n-type	160,000	CF4	39	-	-	O2	3	50	100	600	0.492	68	-	-	-	-
6	100	n-type	160,000	CF4	39	-	-	O2	3	60	100	600	0.597	79	-	-	-	-
7	100	n-type	160,000	CF4	48	-	-	O2	3	40	100	600	0.451	55	-	-	-	-
8	100	n-type	160,000	CF4	48	-	-	O2	3	50	100	600	0.534	56	-	-	-	-
9	100	n-type	160,000	CF4	48	-	-	O2	3	60	100	600	0.614	67	-	-	-	-
Follow-on CF4/O2 RIE Selectivity Study																		
10	111	n-type	360,000	CF4	24	-	-	O2	3	80	70	600	2.615	166	2.178	136	1.648	95
11	111	n-type	360,000	CF4	24	-	-	O2	3	80	100	600	2.246	203	1.992	193	1.545	147
12	111	n-type	360,000	CF4	24	-	-	O2	3	80	130	600	1.586	209	1.645	239	1.634	183
13	111	n-type	360,000	CF4	24	-	-	O2	3	100	70	600	2.361	306	2.899	131	3.197	103
14	111	n-type	360,000	CF4	24	-	-	O2	3	100	100	600	3.064	274	2.447	218	1.773	145
15	111	n-type	360,000	CF4	24	-	-	O2	3	100	130	600	1.962	273	1.678	246	1.809	215
16	111	n-type	360,000	CF4	24	-	-	O2	3	120	70	600	9.282	272	3.056	118	2.464	107
17	111	n-type	360,000	CF4	24	-	-	O2	3	120	100	600	4.183	342	2.630	226	1.779	183
18	111	n-type	360,000	CF4	24	-	-	O2	3	120	130	600	1.684	322	2.291	239	1.999	221
19	111	n-type	360,000	CF4	54	-	-	O2	3	80	70	600	3.125	143	1.894	88	2.070	62
20	111	n-type	360,000	CF4	54	-	-	O2	3	80	100	600	1.139	117	1.262	124	0.903	93
21	111	n-type	360,000	CF4	54	-	-	O2	3	80	130	600	1.117	147	1.168	165	1.128	134
22	111	n-type	360,000	CF4	54	-	-	O2	3	100	70	600	5.001	198	2.472	96	1.786	66
23	111	n-type	360,000	CF4	54	-	-	O2	3	100	100	600	2.548	197	1.949	147	1.374	105
24	111	n-type	360,000	CF4	54	-	-	O2	3	100	130	600	1.964	211	1.632	190	1.335	137
25	111	n-type	360,000	CF4	54	-	-	O2	3	120	70	600	5.628	224	2.542	92	1.327	73
26	111	n-type	360,000	CF4	54	-	-	O2	3	120	100	600	2.397	395	2.234	131	2.141	97
27	111	n-type	360,000	CF4	54	-	-	O2	3	120	130	600	1.651	212	1.733	196	2.483	150
28	111	n-type	360,000	CF4	84	-	-	O2	3	80	70	600	2.374	105	1.432	63	0.660	46
29	111	n-type	360,000	CF4	84	-	-	O2	3	80	100	600	1.549	116	1.334	99	1.108	67
30	111	n-type	360,000	CF4	84	-	-	O2	3	80	130	600	0.859	99	0.793	102	0.770	97
31	111	n-type	360,000	CF4	84	-	-	O2	3	100	70	600	5.929	156	2.030	63	1.684	40
32	111	n-type	360,000	CF4	84	-	-	O2	3	100	100	600	2.013	131	1.687	108	1.186	73
33	111	n-type	360,000	CF4	84	-	-	O2	3	100	130	600	1.507	154	No Data	134	1.168	111
34	111	n-type	360,000	CF4	84	-	-	O2	3	120	70	600	4.406	175	2.416	75	1.384	44
35	111	n-type	360,000	CF4	84	-	-	O2	3	120	100	600	3.597	198	2.192	109	1.486	75
36	111	n-type	360,000	CF4	84	-	-	O2	3	120	130	600	2.241	198	1.690	140	1.610	102
SF6/CHF3/O2 RIE Etch Selectivity Study																		
37	111	n-type	3,750,000	SF6	30	CHF3	6	O2	3	100	50	1440	15.562	160	24.689	171	2.467	146
38	111	n-type	3,750,000	SF6	30	CHF3	12	O2	3	125	100	1440	20.062	448	20.263	447	41.456	457
39	111	n-type	3,750,000	SF6	30	CHF3	18	O2	3	150	150	1440	12.519	595	14.450	596	84.586	560
40	111	n-type	3,750,000	SF6	45	CHF3	6	O2	3	125	150	1440	18.532	822	14.503	784	21.994	846
41	111	n-type	3,750,000	SF6	45	CHF3	12	O2	3	150	50	1440	2.540	16	1.886	36	1.766	17
42	111	n-type	3,750,000	SF6	45	CHF3	18	O2	3	100	100	1440	18.497	359	16.239	354	11.783	388
43	111	n-type	3,750,000	SF6	60	CHF3	6	O2	3	150	100	1440	24.720	171	26.293	181	18.907	173
44	111	n-type	3,750,000	SF6	60	CHF3	12	O2	3	100	150	1440	10.717	693	10.192	626	51.272	770
45	111	n-type	3,750,000	SF6	60	CHF3	18	O2	3	125	50	1440	62.140	41	24.912	54	57.168	50

Appendix B. Additional Results

2.1 Screening CF₄ RIE Selectivity Study

Table 19: Selectivity of each individual unit (3 replicates per treatment) in the screening CF₄ RIE selectivity study.

Pressure	Gas Flow Ratio ($O_2:CF_4$)								
	A (1:10)			B (1:13)			C (1:16)		
1 (40 mTorr)	<u>Unit 2</u>	<u>Unit 20</u>	<u>Unit 6</u>	<u>Unit 23</u>	<u>Unit 25</u>	<u>Unit 9</u>	<u>Unit 3</u>	<u>Unit 15</u>	<u>Unit 28</u>
	0.3396	0.3378	0.3305	0.4281	0.4622	0.4379	0.4394	0.4592	0.4539
2 (50 mTorr)	<u>Unit 26</u>	<u>Unit 11</u>	<u>Unit 5</u>	<u>Unit 29</u>	<u>Unit 17</u>	<u>Unit 7</u>	<u>Unit 14</u>	<u>Unit 30</u>	<u>Unit 8</u>
	0.4739	0.4842	0.4865	0.4724	0.4979	0.5044	0.5166	0.5635	0.5232
3 (60 mTorr)	<u>Unit 21</u>	<u>Unit 13</u>	<u>Unit 4</u>	<u>Unit 12</u>	<u>Unit 31</u>	<u>Unit 27</u>	<u>Unit 22</u>	<u>Unit 18</u>	<u>Unit 10</u>
	0.6129	0.6088	0.6185	0.5978	0.5944	0.5974	0.6218	0.5990	0.6204

Appendix C. Equipment

3.1 Trion Minilock-Phantom III



Figure 52: Trion Minilock-Phantom III RIE/ICP System.

The Trion Minilock-Phantom III RIE/ICP system was used for all etch studies and has the following characteristics and capabilities:

- Reactor: Cathode and anode machined from single aluminum blocks and hard anodized for protection from process chemistries. Can process single wafers or mounted parts 3" to 300mm. Process gases are introduced into the chamber by annular ring or showerhead manifold.
- Automatic matching network: Bottom electrode ensures accurate tuning, low transmission loss, and virtually no RF radiation outside the network. A phase magnitude sensor and amplifiers provide instantaneous feedback for rapid precise tuning.
- Vacuum loadlock: Fully integrated loadlocked delivery system. System includes a robotic arm with direct drive pick and place, reactor isolation valve, and locked chamber for high reliability.
- RF Generator: 600 W, 13.56 MHz solid state RF generator.
- Automatic pressure control: Butterfly pressure control valve operated by the process controller. Provides independent pressure control separate from all other process parameters.
- Gas delivery system: State-of-the-art system accommodating up to eight mass flow controllers and plumbing with surface mount, C-seal technology, and orbital welded VCR fittings.

3.2 Heidelberg μ PG 101 micro pattern generator



Figure 53: Heidelberg μ PG 101 micro pattern generator.

In this study the Heidelberg μ PG 101 mask writer was used to create the etch selectivity mask and in a direct write photolithography application. The μ PG 101 is a micro pattern generator for direct writing applications and low volume mask making. Some of its specifications are listed below.

- Substrates up to 100 x 100 mm²
- Critical dimension resolution of 1 micron
- Multiple data input formats (DXF, CIF, BMP)
- Camera system for alignment
- 375 nm diode laser wavelength
- 18 mW laser source

Appendix D. MATLAB Code

4.1 Selectivity Study DOE and Unit Assignment

```
% Second Selectivity Study
% -----Set up the Treatment Combinations
% ----- %
% Each column is a factor
% Number value corresponds to the level
dff = (fullfact([3 3 3])-1);      % Full factorial with
    3 factor 3 level DOE
treatments = length(dff);        % # of treatments

% ----- Randomize Wafer Pieces
% ----- %
% Dice wafer into its respective Y units
% Run for each type of PR being studied (S1818, SF11+
    S1818, AZ9260)

Units = randperm(X,Y);           % Randomly selects X of the
    Y available units
Uassign = reshape(Units,Z,W);    % Assigns each unit to a
    treatment
Uassign'
```

4.2 Selectivity Calculations

Shown below are the selectivity calculations for Shipley 1818 photoresist in the follow-on CF₄/O₂ selectivity study. Units were assigned to a treatment. Then the process for calculating selectivity outlined in Figure 17 in ??

All selectivity calculations followed this same approach.

```
% Treatment Array
Treatments = [000;001;002;010;011;012;020;021;022;100;101;102;110;111;
112;120;121;122;200;201;202;210;211;212;220;221;222];

% Shipley 1818
S18_U = [26;          % Unit Assigned to Treatment 000
31;          % Unit Assigned to Treatment 001
7;           % Unit Assigned to Treatment 002
30;          % Unit Assigned to Treatment 010
14;          % Unit Assigned to Treatment 011
9;           % Unit Assigned to Treatment 012
6;           % Unit Assigned to Treatment 020
29;          % Unit Assigned to Treatment 021
21;          % Unit Assigned to Treatment 022
5;           % Unit Assigned to Treatment 100
10;          % Unit Assigned to Treatment 101
25;          % Unit Assigned to Treatment 102
36;          % Unit Assigned to Treatment 110
1;           % Unit Assigned to Treatment 111
2;           % Unit Assigned to Treatment 112
13;          % Unit Assigned to Treatment 120
19;          % Unit Assigned to Treatment 121
34;          % Unit Assigned to Treatment 122
3;           % Unit Assigned to Treatment 200
18;          % Unit Assigned to Treatment 201
8;           % Unit Assigned to Treatment 202
28;          % Unit Assigned to Treatment 210
16;          % Unit Assigned to Treatment 211
33;          % Unit Assigned to Treatment 212
20;          % Unit Assigned to Treatment 220
24;          % Unit Assigned to Treatment 221
17];         % Unit Assigned to Treatment 222

% S1818 Initial PR thickness
S18_Pri = [1.9393 1.9236;      % Unit 26
1.9296 1.8797;              % Unit 31
1.878 1.911;                % Unit 7
1.9188 1.9185;              % Unit 30
1.9279 1.8917;              % Unit 14
1.8891 1.8928;              % Unit 9
1.879 1.8673;               % Unit 6
1.928 1.9317;               % Unit 29
1.9451 1.9287;              % Unit 21
1.8724 1.8665;              % Unit 5
1.9317 1.9124;              % Unit 10
1.9089 1.9139;              % Unit 25
1.9372 1.9452;              % Unit 36
1.87 1.8695;                % Unit 1
1.8832 1.8739;              % Unit 2
1.9017 1.9002;              % Unit 13
1.9021 1.9114;              % Unit 19
1.9661 1.9708;              % Unit 34
1.8527 1.8642;              % Unit 3
1.9094 1.9117;              % Unit 18
1.9028 1.9087;              % Unit 8
1.9984 1.9959;              % Unit 28
1.8764 1.8739;              % Unit 16
1.9937 1.9941;              % Unit 33
1.9747 1.9503;              % Unit 20
1.9018 1.9025;              % Unit 24
1.9184 1.9098];             % Unit 17

S18_Pri = mean(S18_Pri,2);    % Avg S1818 Initial PR thickness

table1 = [S18_U S18_Pri];

% S1818 Post Etch Measurements
S18_PE = [2.9796 2.9322;      % Unit 26
3.0228 3.0397;              % Unit 31
2.6547 2.6789;              % Unit 7
4.4266 2.9393;              % Unit 30
3.8015 3.7158;              % Unit 14
3.1942 3.2652;              % Unit 9
4.3777 4.2145;              % Unit 6
4.5483 4.5123;              % Unit 29
3.2595 3.2307;              % Unit 21]
```

```

2.8623 2.8272;      % Unit 5
2.0884 2.0403;      % Unit 10
2.0755 2.0543;      % Unit 25
3.567 3.4771;       % Unit 36
3.0517 3.0834;      % Unit 1
2.9291 2.8983;      % Unit 2
3.8054 3.6766;      % Unit 13
4.2368 4.1766;      % Unit 19
2.8013 2.8096;      % Unit 34
2.4629 2.4708;      % Unit 3
2.3357 2.3076;      % Unit 18
1.5898 1.8963;      % Unit 8
3.3185 3.2613;      % Unit 28
2.5352 2.5353;      % Unit 16
2.4885 2.5347;      % Unit 33
3.3047 3.3229;      % Unit 20
3.3189 3.3506;      % Unit 24
3.0141 3.0017];     % Unit 17

S18_PE = mean(S18_PE,2);      % Avg S18 Post Etch Measurements

% S1818 Final Etch Depth Measurements - Post Clean
S18_SiE =[1.6846 1.6328;      % Unit 26
2.0332 2.0278;      % Unit 31
2.0914 2.0886;      % Unit 7
3.0715 3.0495;      % Unit 30
2.7654 2.7237;      % Unit 14
2.7066 2.7534;      % Unit 9
2.7001 2.7309;      % Unit 6
3.3986 3.4361;      % Unit 29
3.2576 3.1819;      % Unit 21
1.4528 1.4157;      % Unit 5
1.1838 1.1536;      % Unit 10
1.4734 1.4644;      % Unit 25
1.9958 1.9561;      % Unit 36
1.982 1.9611;      % Unit 1
2.1256 2.0918;      % Unit 2
2.299 2.1763;      % Unit 13
3.9724 3.9193;      % Unit 19
2.1257 2.1217;      % Unit 34
1.0528 1.0497;      % Unit 3
1.1705 1.1493;      % Unit 18
.9914 .9945;      % Unit 8
1.5498 1.5603;      % Unit 28
1.3037 1.3197;      % Unit 16
1.5406 1.5378;      % Unit 33
1.7861 1.71;      % Unit 20
1.9799 1.9884;      % Unit 24
1.975 1.975];     % Unit 17

S18_SiE = mean(S18_SiE,2);      % Avg Etch Depth Measurements

% Selectivity calculations
S18_PRf = S18_PE-S18_SiE;      % Post-etch PR Thickness
S18_PRE = S18_PRi-S18_PRf;      % Amount of PR etched
S18_SEL = S18_SiE./S18_PRE;      % Etch Selectivities

S18_SEL_Table = [Treatments S18_SEL];

% Final Selectivities Table
Counter = 1:1:27;
Counter = Counter';
FST = [Counter Treatments S18_SEL AZ_SEL SF11_SEL];

% Sort each treatment by factor for boxplots:

% Gas Flow Ratio
% 0 = 1:8 (O2:CF4)
% 1 = 1:18 (O2:CF4)
% 2 = 1:28 (O2:CF4)
FST_GF0 = FST(1:9,3:5);
FST_GF1 = FST(10:18,3:5);
FST_GF2 = FST(19:27,3:5);

% Averages
FST_GF0_Avg = mean(FST_GF0)
FST_GF1_Avg = mean(FST_GF1)
FST_GF2_Avg = mean(FST_GF2)

% Box Plots
FST_GF = [FST_GF0 FST_GF1 FST_GF2];

% Gas Flow Ratio Box Plot
FST_GF_S1818 = [FST_GF0(:,1) FST_GF1(:,1) FST_GF2(:,1)];
FST_GF_AZ = [FST_GF0(:,2) FST_GF1(:,2) FST_GF2(:,2)];
FST_GF_SF11 = [FST_GF0(:,3) FST_GF1(:,3) FST_GF2(:,3)];

% Pressure

```

```

% 0 = 80mTorr
% 1 = 100mTorr
% 2 = 120mTorr
FST_Pr0 = [FST(1:3,3:5);FST(10:12,3:5);FST(19:21,3:5)];
FST_Pr1 = [FST(4:6,3:5);FST(13:15,3:5);FST(22:24,3:5)];
FST_Pr2 = [FST(7:9,3:5);FST(16:18,3:5);FST(25:27,3:5)];

FST_Pr = [FST_Pr0 FST_Pr1 FST_Pr2];
FST_Pr_S1818 = [FST_Pr0(:,1) FST_Pr1(:,1) FST_Pr2(:,1)];
FST_Pr_AZ = [FST_Pr0(:,2) FST_Pr1(:,2) FST_Pr2(:,2)];
FST_Pr_SF11 = [FST_Pr0(:,3) FST_Pr1(:,3) FST_Pr2(:,3)];

% RF Power
% 0 = 70W
% 1 = 100W
% 2 = 130W
RFP0 = 1:3:27;
RFP1 = 2:3:27;
RFP2 = 3:3:27;
FST_RFP0 = FST([RFP0],3:5);
FST_RFP1 = FST([RFP1],3:5);
FST_RFP2 = FST([RFP2],3:5);

FST_RFP = [FST_RFP0 FST_RFP1 FST_RFP2];
FST_RFP_S1818 = [FST_RFP0(:,1) FST_RFP1(:,1) FST_RFP2(:,1)];
FST_RFP_AZ = [FST_RFP0(:,2) FST_RFP1(:,2) FST_RFP2(:,2)];
FST_RFP_SF11 = [FST_RFP0(:,3) FST_RFP1(:,3) FST_RFP2(:,3)];

```

4.3 Line of Best Fit Calculations for Gas Flow Rate Ratio and Chamber Pressure in Screening CF₄/O₂ RIE Selectivity Study

```
% Line of Best Fit with Pressure on X-Axis
x = [40;50;60];
figure(2)
plot(x,ESR_Avg(:,1),'o')
%xlim([0.9 3.1])
%xticks([1 2 3])
%xticklabels({'40','50','60'})
%xlim([39 61])

coeffs1 = polyfit(x, ESR_Avg(:,1), 1);
% Get fitted values
fittedX1 = linspace(min(x), max(x), 200);
fittedY1 = polyval(coeffs1, fittedX1);
% Plot the fitted line
hold on;
plot(fittedX1, fittedY1);

plot(x,ESR_Avg(:,2),'o')
coeffs2 = polyfit(x, ESR_Avg(:,2), 2);
% Get fitted values
fittedX2 = linspace(min(x), max(x), 200);
fittedY2 = polyval(coeffs2, fittedX2);
% Plot the fitted line
plot(fittedX2, fittedY2);

plot(x,ESR_Avg(:,3),'o')
coeffs3 = polyfit(x, ESR_Avg(:,3), 1);
% Get fitted values
fittedX3 = linspace(min(x), max(x), 200);
fittedY3 = polyval(coeffs3, fittedX3);
% Plot the fitted line
plot(fittedX3, fittedY3);

title('Si:S1818 Selectivity vs. Chamber Pressure')
lgd = legend('1:10 (O2:CF4)', '1:10 Trend Line','1:13 (O2:CF4)', '1:13 Trend Line', '1:16 (O2:CF4)', '1:16 Trend Line');
title(lgd, 'Gas Flow Rate Ratio')
xlabel('Chamber Pressure (mTorr)')
ylabel('Selectivity (Si:S1818)')

%
%e.g. include significant MATLAB Code
```

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