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Los Angeles

Selective and Anisotropic Etching of Metals
through Surface Modification

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy
in Chemical Engineering

by

Owen Watkins

2026

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ABSTRACT OF THE DISSERTATION

Selective and Anisotropic Etching of Metals through Surface Modification

by

Owen Watkins

Doctor of Philosophy in Chemical Engineering

University of California, Los Angeles, 2026

Professor Jane P. Chang, Chair

As demand for computing power and memory continues to increase, continued scaling requires the integration of Ru as a replacement for Cu in the lowest level of metal wiring, and CoFeB for enabling magnetoresistive memory cells. To etch these materials, a systematic approach was taken. In this work, thermochemical analyses were performed to assess the feasibility of each chemistry and guide the experimental work. A combination of modelling, diagnostics, and sample characterization was used to determine the etch mechanisms, enabling selectivity and anisotropy.

A cyclic chemical process with sequential exposure to N_2 , H_2 , and O_2 plasmas was developed to circumvent the isotropic etch profile formed by O_2 plasma without loss of selectivity. RuN was formed in N_2 plasma to act as a passivation layer against O_2 plasma etching of Ru. A hydrogen plasma was able to reduce RuN to Ru, with low energy hydrogen ions enhancing the reduction. The cyclic process yielded an etch rate of 3.6 nm per cycle with ions present, but did

not etch when ions were excluded. The ion-dependent etch was confirmed by etching nano-scale patterned ruthenium samples. Oxygen plasma produced an isotropic etch profile with an etch anisotropy of 4 and a selectivity of 27 with respect to the hard mask, SiO₂. The N₂/O₂ cyclic process increased the anisotropy to 10, but the etch profile was tapered due to passivation by RuN. The N₂/H₂/O₂ cyclic process maintained an anisotropy of 10 while achieving a more vertical etched profile and a selectivity of 16. On nanoscale features, the cyclic process was anisotropic, less dependent on aspect ratio, and maintained a high selectivity versus the hard mask.

To remove CoFeB chemically while circumventing redeposition of less volatile reaction products, atomic layer etching (ALE) of CoFeB was performed using a two-step process. Oxygen plasma was used to increase the oxidation state of the metal, enabling reactions with organic acid vapor to form volatile products. The use of O₂ plasma was found to cause the formation of Co₃O₄, a mixed valence oxide that led to lower etch rate of Co by preventing the formation of Co (II) products. Formic acid or hexafluoroacetylacetone (hfac) were both shown to be able to etch the oxidized CoFeB surface in a controlled manner. The process using formic acid had a lower etch rate, 0.26 nm per cycle, and organic residue remained on the surface, but the selectivity vs. W was effectively infinite. Etching with hfac had a higher etch rate of 0.55 nm per cycle without organic residue on the surface, but the selectivity vs. W was 6 and the surface was enriched with Co.

This work utilized a systematic approach involving thermochemical analysis followed by experimental verification to develop cyclic etching processes for Ru and CoFeB. Surface modification steps were used to induce anisotropy in Ru or control the removal of CoFeB, allowing these materials to be integrated into next-generation devices where control of etch results is critical.

The dissertation of Owen Watkins is approved.

Andrew Kummel

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Jane P. Chang, Committee Chair

University of California, Los Angeles

2026

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PRESENTATIONS

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Watkins, O.,* Simka, H.S., Chang, J.P. Enabling Anisotropic and Selective Etch Through Surface Modification of Ru. *AVS 70th Int. Symposium*, Tampa, FL, November 5, 2024.

Watkins, O.,* Simka, H.S., Chang, J.P. Anisotropic and Selective Atomic Layer Etching of Ruthenium. *AVS 69th Int. Symposium*, Portland, OR, November 6, 2023.

Chang J.P., Watkins, O.* Engineering chemical processes for sustainability in patterning nano-electronics. *SPIE Adv. Lithograph + Patterning*, San Jose, CA, March 2, 2023.

*Presenter

Chapter 1. Introduction

In order to address the scaling down of semiconductor devices, novel materials are being introduced to overcome limitations caused by the shrinking of critical dimensions. In addition to having satisfactory material properties, these next-generation metals must have patterning processes that enable their use. Ruthenium has the potential to replace Cu at the sub 10 nm scale due to its lower electron mean free path and greater resistance to electromigration and thermal diffusion. For Ru to be a viable candidate, it must be etched in an anisotropic and selective manner at nanoscale dimensions, allowing it to be integrated into back-end-of-line patterning schemes. CoFeB, a magnetic alloy, has promise as the magnetoresistive layers used in magnetic tunnel junctions that can be used as non-volatile random-access memory. Due to the sensitivity of these devices, an etching process must be developed that does not result in redeposition, which can cause shorts, and preserves the properties of the material, which can be easily degraded through compositional and structural changes to the exposed surfaces.

1.1 Novel Metals for Next-Generation Technologies

To meet the ever-growing demands for computational power, the density of semiconductor devices must continually increase. As the size of devices drops closer and closer to their physical limit, the complexity of design and fabrication balloons as new solutions in turn create their own problems to be solved. One limiting factor for many areas of new technology development is the material constants, such as resistivity and capacitance. As dimensions shrink, in many cases material properties are the only way to overcome the barriers that arise. In the back-end-of-line (BEOL), metal lines, or interconnects, transmit signals between the millions or billions of transistors that make up today's devices. As the dimensions of the smallest interconnects in the

layer directly above the transistors must match the dimensions of the transistors themselves, the widths of the metal lines are now in the tens of nanometers. At these scales, scattering effects and additional layers have rendered Cu obsolete, with new metals required to take its place in the lowest metal layers. Among these is Ruthenium, which promises improved resistivity and novel patterning schemes at the 10 nm scale. For Ru to be used for this application, an etching process with strict requirements for selectivity and anisotropy must be developed.

In the field of memory, magnetoresistive memory (MRAM) has potential for multiple applications thanks to being nonvolatile and random-access. While established memory technology, such as NAND flash and DRAM, are lower in cost and higher in density, MRAM could be used as static RAM and in embedded devices with low power consumption. The critical device used in MRAM is the magnetic tunnel junction (MTJ), which stores information by being in either a high resistance or low resistance state based on the alignment of two magnetic layers. The material properties of this magnetic layer have the highest importance for the viability of MRAM, as they define the reliability and energy cost of switching, long-term stability, and ratio between on and off states. A ternary alloy, CoFeB, has been identified as the optimal material for this purpose, surpassing other elemental metals and alloys, enabling a high resistivity ratio. The complete stack of materials in a MTJ is complex, and currently is patterned by physical sputtering with Ar ions. However, as the material properties are critical to the device performance, and even small amounts of redeposition can cause shorts and degraded material properties, a novel etching process is needed for the etching of CoFeB.

1.1.1 Ru Interconnects for Scaling Beyond Cu

At the lowest level of a device are the transistors, the individual logic circuits that form the basis of computing. As they have shrunk, new materials such as HfO_2 gates have been introduced, new layouts are incorporated to counteract the effects of scaling, and new deposition and etching techniques have been developed to realize these designs. As transistors shrink, so too must the infrastructure that surrounds them. After the transistors have been formed, processes form the interconnects that transmit signals from the nanoscale transistors to the macroscale contacts. In the BEOL, interconnects are made of metals that minimize resistance, while the insulating surrounding materials are chosen to minimize capacitance. The delay in switching a line from 0 (power off) to 1 (power on) is represented by

$$V(t) = V_0(1 - \exp(-t/\tau)), \quad \tau = RC \quad (1.1)$$

where R is resistance and C is capacitance, with a lower value of τ resulting in a quicker increase to the voltage (Rubinstein et al., 1983). This RC delay must be minimized to allow logic to run at frequencies in the GHz range to meet the demands for clock speed in modern processors.

As transistors shrink, the cross-sectional area of interconnect wires shrinks correspondingly, but the overall lengths of the interconnects are not scaled down. This causes the RC delay to increase as resistance and capacitance correspond to the dimensions of the wire:

$$R = \rho l/hw, \quad C = k\epsilon_0 lh/d, \quad RC = \rho k\epsilon_0(l^2/wd) \quad (1.2)$$

where ρ and k are two material-specific constants, the resistivity and relative permittivity (dielectric constant), ϵ_0 is the vacuum permittivity, and l , h , and w are the length, width and height of the wire, while d is the distance between adjacent wires, as illustrated in Figure 1.1. From this,

it can be seen that increasing length and decreasing the spacing of metal lines and interlayer dielectric (ILD) leads to increased RC delay. Since the shrinking of dimensions is required for scaling, the only way left to reduce the RC delay is to use materials with as low ρ and κ as possible.

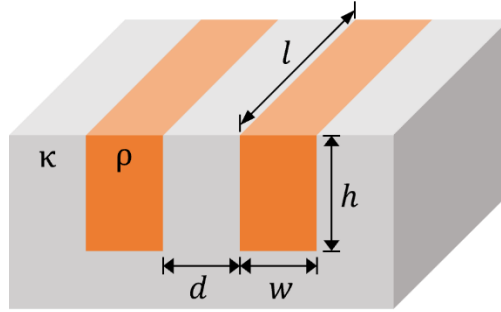


Figure 1.1. Diagram of the dimensions of interconnect lines (orange) surrounded by dielectric (gray).

Beyond the material properties, there are processing and reliability concerns as well. One phenomenon that must be accounted for in the design of interconnects is electromigration, where atoms in a metal flow with the electron current when an electric field is applied. The flux of atoms caused by electromigration is described as

$$J = \frac{DN}{kT} \left(Z^* E e - \Omega \frac{\partial \sigma}{\partial x} \right) \quad (1.3)$$

where D is the diffusivity, N is the atomic density, k is Boltzmann's constant and T is temperature, Z^* is the effective charge number, E is the electric field, e is the charge of an electron, Ω is the atomic volume, and $\partial \sigma / \partial x$ is the stress gradient along the wire (Blech & Herring, 1976; Hau-Riege, 2004). In areas such as the interface between a via and line below the net flux is less than zero, so voiding occurs as the metal is removed from that area. In other sections, the net flux is correspondingly above zero, causing extrusion and therefore short circuiting to occur. Both of these faults are critical to avoid, making electromigration a primary concern.

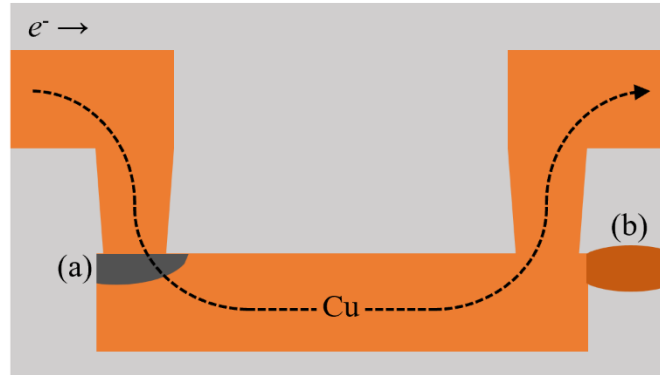


Figure 1.2. Examples of defects caused by electromigration. (a) Voiding at the via-line interface causing open circuit failure. (b) Extrusion into the ILD causing short circuit failure.

While aluminum was originally used as the interconnect metal due to its low resistivity of $2.7 \mu\Omega\text{-cm}$ and ease of patterning, shrinking of interconnects below micron-scale required the adoption of a new material by the beginning of the 21st century – copper. With a bulk resistivity of $1.7 \mu\Omega\text{-cm}$, Cu replaced Al in interconnects, reducing the RC delay ("Electrical Resistivity of Pure Elemental Metals," 2026). Al was also susceptible to electromigration, while Cu was suspected to be less affected. However, the switch to Cu required a change to the fabrication process, as it was not as easily dry etched as Al. Instead of a subtractive process, where blanket Al films were patterned and etched into the lines, then dielectric was deposited to fill the interlayer space, it was necessary to pattern then dielectric, then electrodeposit Cu.

This new Cu process, dual damascene, relied on chemical-mechanical planarization (CMP) to remove the excess Cu, rather than etching. Despite the additional processing requirements as outlined in Figure 1.3, the dual damascene process was successful in transitioning the interconnect metal of choice to Cu. As transistors continued to scale down to sub 100 nm sizes, the Cu interconnects kept RC delay down in conjunction with the development of low- k SiCOH-based materials used as the surrounding dielectric.

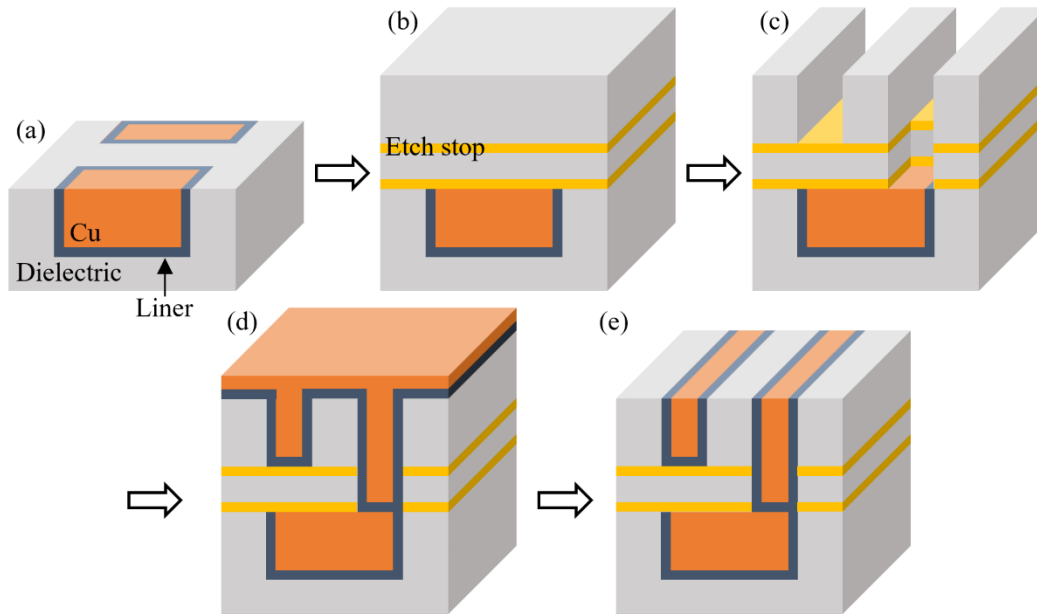


Figure 1.3. Simplified schematic of the dual damascene process. (a) Initially, Cu lines from the previous level have been patterned. (b) Dielectric and etch stop layers are deposited. (c) Dielectric is patterned for the next level of interconnects, and vias are etched to expose the previous Cu layer. (d) After the liner is conformally deposited, Cu is electroplated, filling the vias and lines, and coats the entire surface. (e) Chemical-mechanical planarization removes the surface Cu, leaving the Cu present in the trenches and vias.

As scaling continued and new transistor designs, such as fin and gate-all-around (GAA), were introduced to maximize gate contact area, RC delay became a more pressing issue. While Cu has some of the lowest bulk resistivity, as the cross-sectional area of the interconnect wires shrunk, the overall resistivity increased due to electron scattering effects, as illustrated in Figure 1.4. Additionally, Cu requires both a seed layer for conformal electrodeposition and a barrier layer to prevent electromigration and eventual shorting of neighboring wires. These additional layers were made of more resistive materials, such as TiN, Ta, and/or TaN, making the effective area of the wires even smaller.

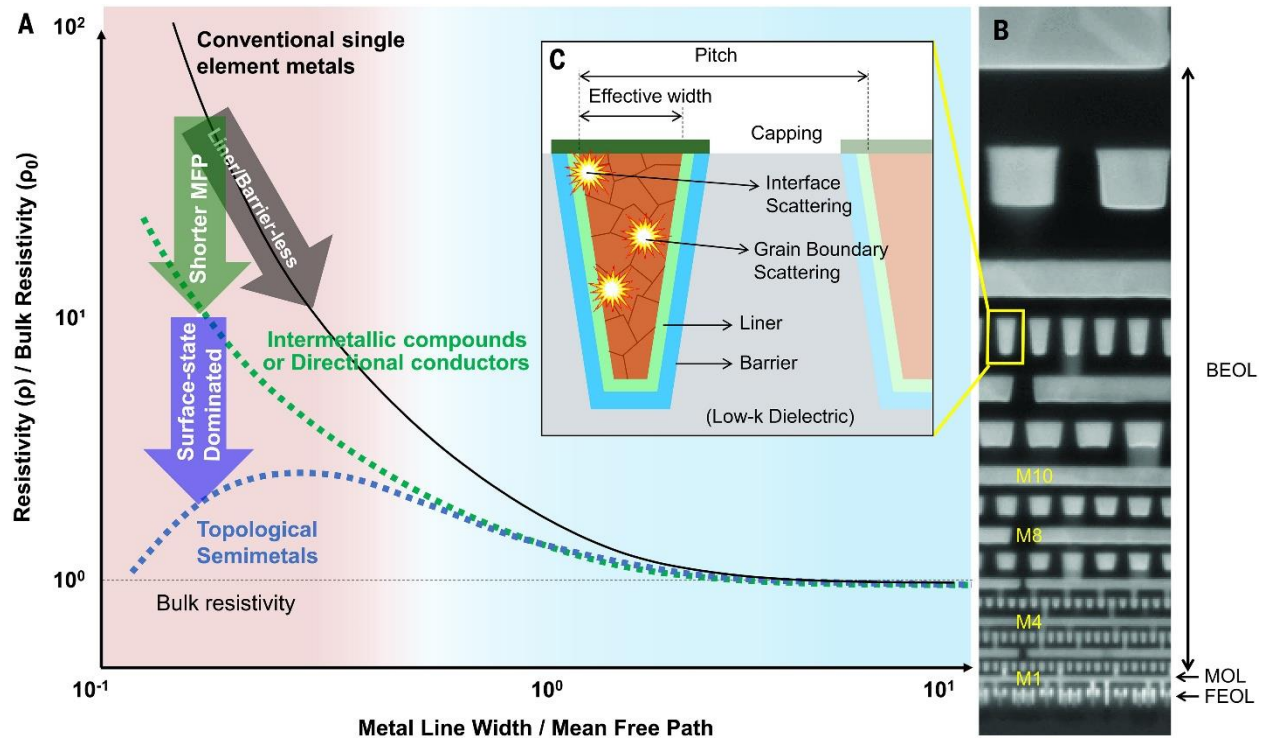


Figure 1.4. (a) The resistivity of metals increases exponentially as line widths reach tens of nm, such as in the M1 layer, the lowest and smallest layer of the BEOL, shown in (b). (c) The increase in resistivity is due to electron scattering effects, as well as reductions to the effective width from liners and barriers. Taken from (Kim et al., 2024).

The limitations of Cu at the 10 nm scale led to a search for potential replacement metals that have lower effective resistivity. Because Cu was still a viable metal for larger interconnects, only the lowest 1-2 levels of metallization would be replaced, while Cu could still be used for the remaining layers. This meant that the metal would not need a lower bulk resistivity as long as it had more favorable properties at the nanoscale. Additionally, to reduce the burden on scaling placed by the barrier layer, a metal that was less prone to electromigration would provide a further boost to resistivity.

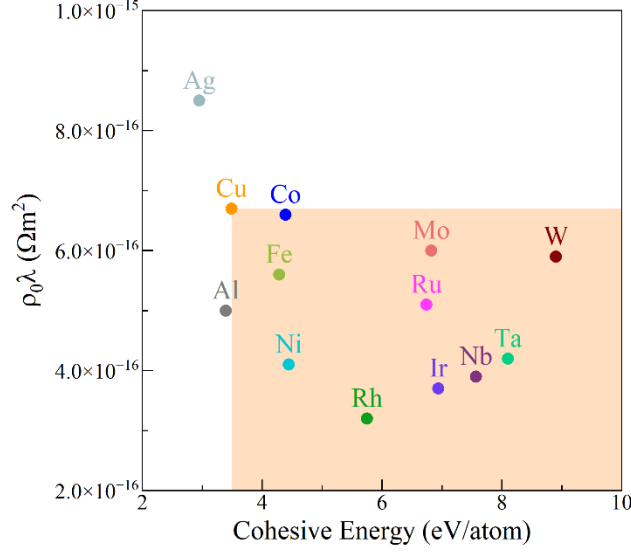


Figure 1.5. Potential metals to replace Cu by their resistivity-mean free path product, which approximates nanoscale resistivity, and cohesive energy, which approximates resistance to electromigration. The shaded box denotes the region where both values are an improvement vs. Cu. Despite their low bulk resistivity, metals such as Ag, Cu, and Al have a larger mean free path and lower cohesive energy, which leads to electron scattering effects and electromigration, respectively.

To determine a figure of merit for minimizing resistivity, an approximation of resistivity accounting for electron scattering at the interface and at grain boundaries was used

$$\rho = \rho_0 + \rho_0\lambda \frac{3(w+h)}{8wh} (1-p) + \rho_0\lambda \frac{3R}{2D(1-R)} \quad (1.4)$$

Where ρ_0 is the bulk resistivity, λ is the mean free path of electrons in the material, D is the grain size, p is the fraction of specular surface scattering, and R is the fraction of backscattered electrons at grain boundaries (Gall, 2020; Mayadas & Shatzkes, 1970; Sondheimer, 1952). From this equation, it can be seen that the deviation from the bulk resistivity is linearly related to $\rho_0\lambda$, making it a simple figure of merit for screening candidate metals.

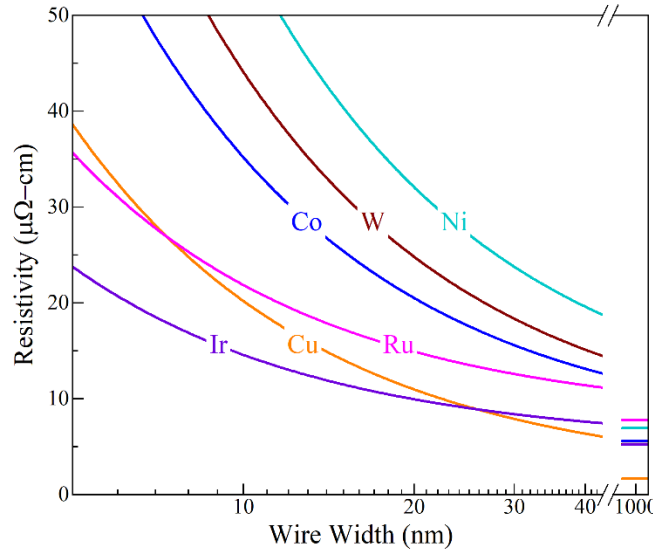


Figure 1.6. Resistivity of select metals as a function of width for a square wire with no barrier layer. As the dimensions of the wire drop below 7 nm, Ru becomes less resistive than Cu, despite its much higher bulk resistivity. Figure adapted from (Gall, 2020).

An additional consideration for interconnect materials is their resistance to electromigration. While Cu represented an improvement over Al, it was still susceptible to electromigration. As Cu diffuses into Si quite easily to form Cu silicides such as Cu_3Si at temperatures as low as 200°C , reliability of Cu directly deposited on Si and Si-based dielectric is poor (Cros et al., 1990). Because elevated temperatures are needed later in processing and electromigration during normal device operation is unavoidable, Cu requires a barrier layer that inhibits diffusion. This diffusion layer is commonly composed of Ta/TaN, though Ru is potentially another candidate. In general, the diffusion layer is much more resistive than Cu, resulting in the effective shrinking of the Cu wire cross-section. As the size of interconnects decreases, the barrier layer stays the same thickness, taking up an ever-larger portion of the interconnect wire and further reducing the effective resistivity of Cu. As Ru is less susceptible to electromigration and the

formation of Ru silicides, thinner barrier or barrierless schemes may be possible. Compared to Cu with a 2 nm barrier in Figure 1.7, barrierless Ru is less resistive at widths of 11 nm or below.

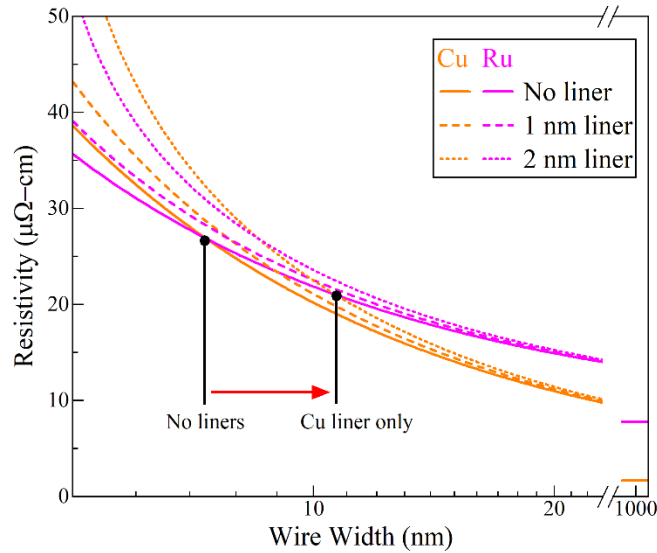


Figure 1.7. Resistivity of Cu and Ru as a function of width for square wires with varying thickness of nonconductive liner layers. When Cu wires require a liner layer, the breakeven width for barrierless Ru is even higher.

Since interconnect layers stretch from the nano- to micro- to millimeter scale, Ru cannot entirely replace Cu, as the latter's lower bulk resistivity and established processing method are still better than Ru at most scales. At the 10 nm scale, new processing schemes have been developed to take advantage of Ru's improved resistivity, as well as other beneficial properties. While the dual damascene scheme was developed to compensate for the lack of etching processes for Cu, Ru has chemistry that enables it to be subtractively etched. This would allow the Ru to be deposited prior to the interlayer dielectric, then etched to form the lines, rather than by conformal deposition, as shown in Figure 1.8. To subtractively etch Ru, a process must be developed that is able to transfer the pattern from the hard mask by etching trenches into the Ru film without damaging the Ru sidewalls or the hard mask itself.

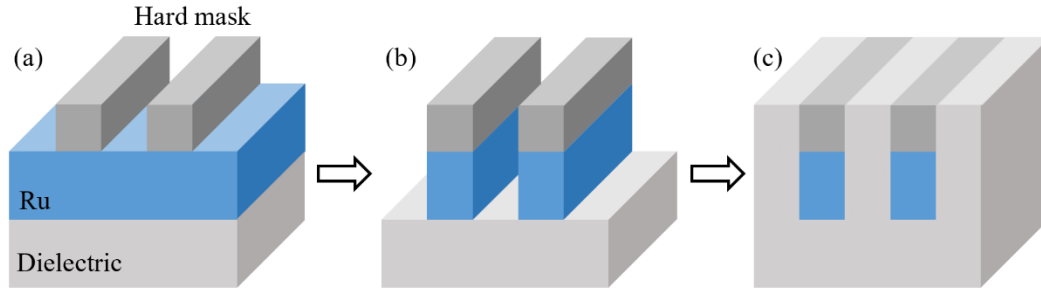


Figure 1.8. Simplified schematic of the Ru subtracting etching process (a) Initially, a typically Si_3N_4 or SiO_2 has been patterned. (b) Ru is etched subtractively to form the interconnect lines. (c) Interlayer dielectric is deposited in between the Ru lines.

1.1.2 Role of CoFeB in Enabling Magnetoresistive RAM

Within the field of semiconductor device manufacturing, much focus has placed on logic due to the importance of scaling down transistors to increase computing power. However, demands for memory are simultaneously growing with a similar need for scaling while maintaining reliability and speed. In particular, two key characteristics define the types of memory in use today – volatility and random-access. Non-volatile memory (NVM) does not require continuous power to retain the memory state. Random-access memory (RAM) does not have read/write speed dependence on the position of a given bit. Naturally, NVM is used for storage – hard drives, solid-state drives (SSDs), and flash drives, while RAM is used to store working data that must be accessed quickly. State-of-the-art memory in all forms uses MOSFETs as their basis, with non-volatile flash memory stored in electrically insulated floating gates, while both static and dynamic RAM use memory gates.

An alternative form of non-volatile memory that has been proposed is magnetoresistive RAM (MRAM), which stores data in the form of magnetization of a ferroelectric layer. Since the magnetization does not require power to maintain, it is non-volatile, and a cell can be formed by

combination with a single transistor. This technology promises both non-volatility and random-access, giving it a wide variety of potential applications should it be able to reach necessary benchmarks for speed, density, reliability, and cost efficiency. As a replacement for flash memory, it promises higher numbers of write cycles, and low power. New advances in NAND flash memory (the industry standard for storage such as SSDs), such as 3D NAND architecture, mean that MRAM is unlikely to replace it. However, MRAM may be able to compete with NOR flash memory, which is random-access, but with lower density and higher power consumption compared to NAND flash. In addition, MRAM is comparable to static RAM (SRAM), which is a type of volatile memory used in application such as cache for CPUs, where high speed is the greatest priority at the cost of lower density, as 6 transistors must be used for a single memory cell. (IEEE, 2024).

Table 1.1. Summary of memory types currently in production (IEEE, 2024). Non-volatile memory does not require power to retain data. Random-access memory can be accessed in any order without significant variation in read time.

Memory	Non-Volatile	Random-Access	Applications
NAND Flash	Yes	No	SSDs, flash drives
NOR Flash	Yes	Yes	Embedded devices, boot instructions
DRAM	No	Yes	Main memory
SRAM	No	Yes	CPU Cache
MRAM	Yes	Yes	Low power embedded devices, IoT, cache

Initial MRAM designs used two ferroelectric layers with an interposed insulating layer to form a magnetic tunnel junction (MTJ). One of the ferroelectric layers, the reference or fixed layer, was magnetized in a certain orientation. The other, the free layer, was magnetized to be either parallel or antiparallel to the fixed layer, as shown in Figure 1.9. In the parallel configuration, the

spins of electrons in each layer are aligned, and the resistance across the two layers drops due to the giant magnetoresistance effect, while in the antiparallel configuration, the resistance is much higher (Baibich et al., 1988; Binasch et al., 1989). By measuring the resistance through the cell, the memory could be read as either “1” (parallel state) or “0” (antiparallel state). By switching the magnetization of the free layer, the memory could be written. The defining value for MTJs used in MRAM is the tunnel magnetoresistance ratio, $TMR = (R_{AP} - R_P)/R_P$. This ratio needs to be sufficiently high to be able to distinguish between the two states without read error.

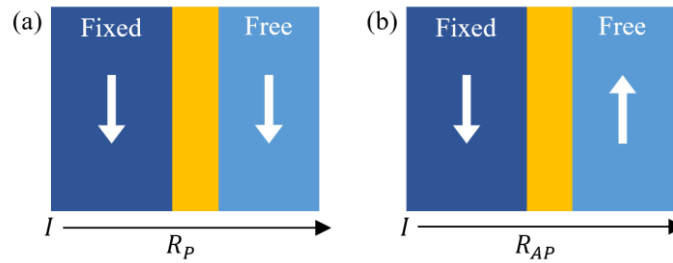


Figure 1.9. Diagram of magnetic transfer junctions in the (a) parallel and (b) antiparallel configurations. Due to the giant magnetoresistance effect, $R_P \ll R_{AP}$.

Despite the promise of MRAM, the requirement of inducing a magnetic field to switch the bit state of the MTJ limited the scalability of the device as it required a high current to write to the device (Apalkov et al., 2013). The discovery of spin-transfer in MTJ was crucial to providing a new pathway to viability for MRAM devices. Spin-transfer is a process that allows the alignment of the free layer to be switched by flowing current through the MTJ (Slonczewski, 1996). As electrons pass through the reference layer, the current becomes polarized as electrons with spin parallel to the electrons in the fixed layer are more likely to tunnel through the insulating layer, and in the free layer, change the alignment of electrons to the parallel state with spin-transfer torque (STT). If sufficient current is instead flowed through the free layer (but not enough to affect the

alignment of the thicker fixed layer), scattered electrons from the interface with the fixed layer are polarized in the antiparallel direction, passing the polarization onto the free layer. Using STT as the write method, STT-MRAM could be fabricated with memory cells as simple as a single transistor and MTJ, as shown in Figure 1.10, similar to the transistor and capacitor design of DRAM (Cai et al., 2021).

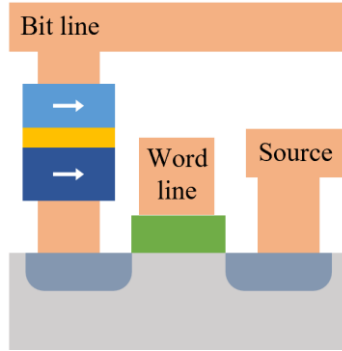


Figure 1.10. Diagram of a STT-MRAM cell. When the word line is activated to allow current to pass through the transistor, the MTJ can be written to by passing a current greater than the threshold current through the bit line to the source or vice versa. By passing a lower current, the MTJ could be read by determining its resistance.

Further improvements to the performance of MTJs focused on improving the TMR as well as thermal stability and threshold current. The thermal stability, Δ , is a function of the energy barrier, E , and temperature,

$$\Delta = E/kT, \quad E = M_s H_K v / 2 \quad (1.5)$$

where M_s is the saturation magnetization, H_K is the anisotropy field, and v is the free layer volume.

The threshold current, I_c , is equal to

$$I_c = \alpha \frac{\gamma e}{\mu_B g} M_s H_K v = 2\alpha \frac{\gamma e}{\mu_B g} E \quad (1.6)$$

where α is the Gilbert damping constant, γ is the gyromagnetic ratio, e is the charge of an electron, μ_B is the Bohr magneton, and g is the spin polarization factor (Slonczewski, 2002). The anisotropy field, H_K , is dependent on the direction of magnetization relative to the plane of the MTJ. In-plane MTJs, as depicted above in Figure 1.9, have a larger anisotropy field, $H_K = H_{K\parallel} + 2\pi M_s$, than perpendicular MTJs, $H_K = H_{K\perp} - 4\pi M_s$, allowing for a lower threshold current given other values remaining equal. While this would also lower the thermal stability from $E = M_s H_{K\parallel} v/2$ to $E = M_s (H_{K\perp} - 4\pi M_s) v/2$, the $2\pi M_s$ term no longer contributes to the threshold current. This perpendicular condition was therefore preferred for scaling given materials with constants sufficient to maintain high thermal stability and low threshold current could be found (Mangin et al., 2006).

While a variety of metals and alloys involving Fe, Co, and Ni were investigated, the material requirements for the free and fixed layers in MTJ were strict. A low damping coefficient was necessary to reduce the threshold current for writing, as well as a high degree of spin polarization (the difference between spin-up and -down density of states at the Fermi level). CoFe and CoFeB alloys were already known to be good ferromagnetic materials for in-plane MTJs, and were subsequently found to demonstrate perpendicular anisotropy at certain thicknesses when used with a MgO barrier layer, resulting in a TMR of over 120% (Ikeda et al., 2010). This breakthrough led to the further development of MTJs for use in STT-MRAM with CoFeB/MgO/CoFeB as the material of choice.

The MTJ stack includes a variety of materials, including CoFeB and MgO tunneling barrier, as well as metals including Ru, Ta, and W that are used for spacing, pinning the reference layer magnetization, and as seed layers. This makes patterning a challenge, as processing these

materials alone can be difficult. In particular, the etching of the CoFeB layers is a problem, as the magnetic properties that enable MTJs are sensitive and can easily be degraded by the patterning process. Conventionally, ion beam milling has been used to pattern the MTJ stack, as it is a purely physical process, meaning that any differences in selectivity can be overcome with sufficient ion energy and without the worry of chemical degradation at the sidewall of the stack. However, as the products of ion beam milling are inherently nonvolatile metals, they readily redeposit on the sidewall, causing shorts. Furthermore, the inherent limits to selectivity mean that a thick hard mask is required.

Etching of CoFeB with chemical means has primarily been done with RIE and ALE. Reactive ion etching combines the benefits of physical sputtering-based processes, such as anisotropy, while resulting in enhanced volatility of products, reducing redeposition. Depending on the chemistry, the volatility of the products may still be low, and any chemical change to the sidewall during etching can remain, leading to degradation of the properties of the layer. For CoFeB, in particular, damage can lead to large increases to the magnetic coercivity, the strength of the magnetic field required to switch the magnetization. The formation of a modified sidewall layer can additionally reduce the effective size of the MTJ if it is weakly or non-magnetic and cannot contribute to the magnetoresistance effect.

While halogens are a common reactive species for RIE, both Co and Fe do not form very volatile species with either Cl or F. In particular, while the boiling point of FeCl_3 is 316°C , for CoCl_2 it is 1049°C , and higher for F-based compounds (Islam et al., 2020). This lack of volatility leads to significant amounts of Cl residue on the surface, degrading the coercivity of the film. While subsequent H_2 plasma exposure was able to reduce Co and Fe chlorides on the surface, the

coercivity was not fully recovered (Altieri et al., 2019). Alternative carbon-based plasma etching processes have been explored, as $\text{Co}_2(\text{CO})_8$ and $\text{Fe}(\text{CO})_5$ are more volatile than their halide counterparts, with boiling points of 52 and 103°C, respectively. In conjunction with Ar, CH_4/O_2 , CH_3OH , CH_3COOH , or CO/NH_3 have been tested (Garay et al., 2015; Kim et al., 2012; Park et al., 2011; Xiao et al., 2011). While all these chemistries have been shown to etch, they leave oxidized Co and Fe on the surface, and their etch rates are low without a large percentage of Ar to facilitate physical etching.

Atomic layer etching of CoFeB provides an alternative that avoid much of the issues with ion-based patterning. Since etching is purely chemical, any products would be volatile enough to avoid redeposition, and selectivity vs. hard mask or underlying layers can be much higher. For ALE in particular, the self-limiting nature of the process can result in less damage to the exposed CoFeB surface or sidewalls. Since CoFeB layer thickness in the MTJ stack is low, the downsides of ALE, such as low etch rate and isotropic etching can be ameliorated. The major obstacle to ALE of CoFeB is finding chemistry that is self-limiting, effective at etching both Co and Fe, and does not leave surface damage.

1.2 Plasma Etching

A common technique for etching thin films is reactive ion etching (RIE), which utilizes plasma to form reactive ion and radical species that use a combination of physical-based sputtering and chemical reactions to remove material from the surface in a controlled manner. By supplying external power, such as from an inductive coil, to a gas, electrons are energized, colliding with molecular and atomic species to form radicals and ions. While these species are normally energetically unfavorable and recombine to lower states, in a plasma, they are continuously

formed, creating a metastable composition of unstable, and therefore more reactive species. Input parameters to the plasma, including power, pressure, feed gas composition allow control over the resultant composition of reactive species, in turn allowing for control over the reactions that occur on the target surface. Increasing power results in a greater extent of ionization, increasing the plasma density, which is the concentration of electrons in the plasma. Since the vast majority of ions in a plasma have a single positive charge, the density of ions is equivalent to the number of free electrons, a condition known as quasineutrality. As the number of electrons increases, dissociation of molecular species into fragments, or radicals, in turn increases. As the pressure of the plasma decreases the mean free path of an electron increases, as at lower densities collisions are less likely. The lower mean free path results in a higher electron temperature, as energy losses from collisions are reduced. In a plasma the temperature of electrons becomes decoupled from neutral species, exceeding 1 eV ($\sim 11,605$ K), while “cold” neutral species generally have temperatures below 1,000 K. The electron temperature represents the kinetic energy of electrons, which is a distribution, rather than a uniform value. While real plasmas are complex, a common assumption is that electrons’ energy follows a Maxwell-Boltzmann distribution,

$$f(v) = \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{m}{kT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right) \quad (1.7)$$

where m is the mass of the particle, k is the Boltzmann constant (8.617×10^{-5} eV/K), T is the temperature, and v is the speed of a particle. The root mean square thermal velocity is therefore

$$\langle v^2 \rangle = \frac{\int_0^\infty v^2 \cdot f(v) dv}{\int_0^\infty f(v) dv} = \frac{2kT}{m} \frac{\Gamma(5/2)}{\Gamma(3/2)} = \frac{3kT}{m}, \quad v_{RMS} = \sqrt{\frac{3kT}{m}} \quad (1.8)$$

and the electron temperature in a plasma is related to the mean kinetic energy, $\langle E \rangle = \frac{3}{2}kT$. The distribution of energy can be derived from equation 1.71.7 using $v = \sqrt{2E/m}$ and $dv = dE/mv$,

$$f(E) = 2 \left(\frac{E}{\pi} \right)^{1/2} \left(\frac{1}{kT} \right)^{3/2} \exp \left(-\frac{E}{kT} \right) \quad (1.9)$$

resulting in an expression that is independent of the particle mass. The distribution is plotted in Figure 1.11 as a function of electron temperature in eV.

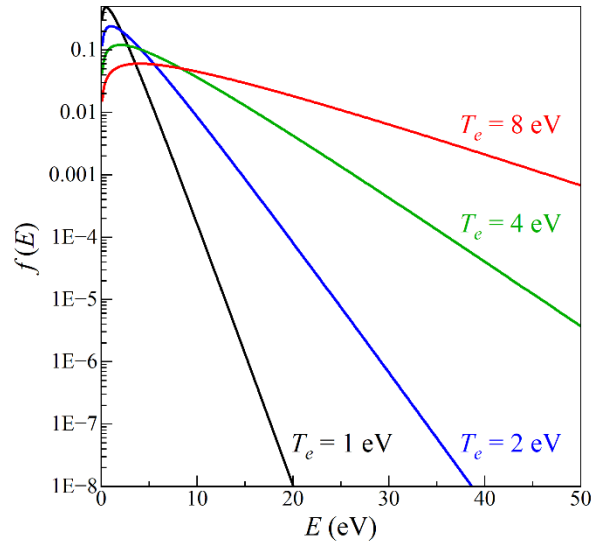


Figure 1.11. Maxwell-Boltzmann probability distribution function of electron energy over a range of electron temperatures, T_e , calculated using equation 1.9. As the electron temperature increases, the number of electrons with energy high enough (>10) to cause ionization or dissociation increases by over an order of magnitude.

As the electron temperature increases, the distribution shifts so that significantly more electrons have energy greater than the threshold energy for dissociation and ionization of molecular and atomic species in the plasma. Threshold energy for selected species is listed in Table 1.2.

Table 1.2. Threshold energy for electron collision with species used in experimental section of this work.

Species	Collision Type	Reaction	Threshold energy (eV)
N ₂	Dissociation	$\text{N}_2 + e^- \rightarrow 2\text{N} + e^-$	9.76
N ₂	Ionization	$\text{N}_2 + e^- \rightarrow \text{N}_2^+ + e^-$	15.58
N	Ionization	$\text{N} + e^- \rightarrow \text{N}^+ + e^-$	14.54
H ₂	Dissociation	$\text{H}_2 + e^- \rightarrow 2\text{H} + e^-$	4.51
H ₂	Ionization	$\text{H}_2 + e^- \rightarrow \text{H}_2^+ + e^-$	15.43
H	Ionization	$\text{H} + e^- \rightarrow \text{H}^+ + e^-$	13.60
O ₂	Dissociation	$\text{O}_2 + e^- \rightarrow 2\text{O} + e^-$	5.16
O ₂	Ionization	$\text{O}_2 + e^- \rightarrow \text{O}_2^+ + e^-$	12.07
O	Ionization	$\text{O} + e^- \rightarrow \text{O}^+ + e^-$	13.62
Ar	Ionization	$\text{Ar} + e^- \rightarrow \text{Ar}^+ + e^-$	15.76

Since ions and radicals are the primary etchant species due to their greater reactivity compared to molecular species, the electron temperature and plasma density are integral to the overall etching process. While the plasma composition can only be controlled indirectly through parameters such as the plasma power and pressure, the energy of ions striking the surface is directly influenced by the potential difference between the plasma and surface. By applying a negative bias, positive ions are accelerated towards the surface, and with sufficient kinetic energy are able to break bonds, physically ejecting material from the surface. This process is known as sputtering, and occurs independently of chemical etching, though oftentimes chemical and physical etching are used synergistically as the basis for RIE. In RIE, reactive species form volatile product molecules on the target surface, while physical sputtering helps desorb the products, enhancing the etch rate. Without ion bombardment, the etch rate is limited by the chemical reaction and kinetic

processes, while without chemical reactions, sputtering results in nonvolatile species that are quick to redeposit.

1.3 O₂ Plasma Etching of Ru

To satisfy the requirements for integration into the back-end-of-line, Ru must be subtractively etched at sub-10 nm dimensions with aspect ratios as high as six. At this scale, there is little margin-of-error for pattern transfer in etching, as small changes to the line dimensions can cause increases to resistivity or misalignment of subsequent layers. Figure 1.12 demonstrates some of the possible issues with post-etching profiles.

One primary requirement for the patterning process is anisotropy. After the hard mask is patterned, the Ru etch process must only etch vertically, while leaving any Ru underneath the hard mask intact in order to preserve the pattern. Inherently, chemical-based etching is isotropic, as reactant particles can just as easily travel to the sidewall as they can to the bottom of the trench. To induce anisotropy, it is then necessary to improve the ratio of vertical to lateral etching either by enhancing the vertical etch rate or inhibiting the lateral etch rate.

Similarly, the selectivity between Ru itself and the hard mask is important, as excessive etching of the hard mask can result in distortion of the pattern, either through lateral etching causing shrinkage of the feature, or redeposition causing enlargement. To ameliorate the effects of low selectivity, the hard mask can be made thicker, but this results in greater aspect ratio of the features as a whole.

The dependence of etch rate on aspect ratio is another important consideration. The aspect ratio of lines is expected to increase as the width of wires shrinks, but the height of wires does not

need to shrink in response. As aspect ratio increases, the flux of reactants into the trench decreases, as particles entering at oblique angles become more likely to collide with the sidewall than at the etch front. While ions are less affected by this phenomenon due to having a sharp angular momentum distribution centered around the surface normal, the lower flux of neutral species lowers the etch rate, making the etch rate dependent on aspect ratio, and therefore feature size.

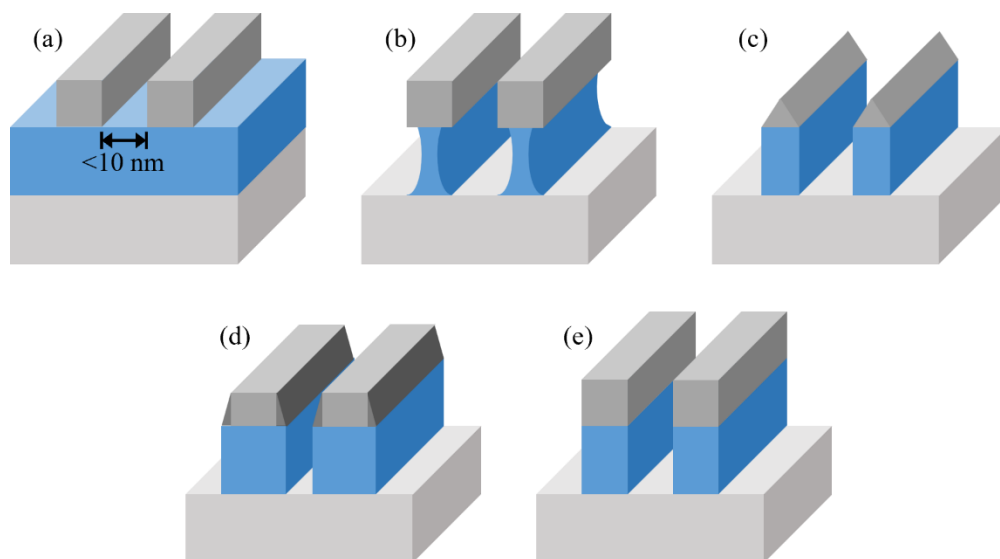


Figure 1.12. Schematic of Ru patterning profiles. (a) Ru with patterned hard mask prior to etching. (b) Ru profile after isotropic etch where the lines have shrunk due to lateral etching. (c) Ru profile after nonselective etch where the hard mask has been etched. (d) Ru profile after non selective etch where redeposition of the hard mask on the sidewall has enlarged the Ru lines. (e) Ideal Ru etch profile with vertical sidewall and no hard mask damage.

As the etching of Ru is primarily to enable subtractive etching schemes for the back-end-of-line, specific patterning steps have additional requirements needed to minimize potential error or defects. A controllable process that can partially etch through a film can be used to recess lines prior to deposition of the next layer to minimize edge placement errors, or for the formation of vias through the partial etch of lines.

Reactive ion etching is a common and effective technique for etching, as reactant and surface chemistry can be used to provide selectivity for one material over another, while the directional bombardment of ions results in anisotropy. For many metals, this product is halogen-based as metal fluorides and/or chlorides are often volatile. By exposing metals to a F_2 or Cl_2 plasma, reactive radicals and ions are formed, and chemical etching reactions occur on the surface, and the desorption of products is enhanced by physical bombardment by ions. However, Ru does not form a very volatile product with F or Cl, with the most volatile product being RuF_5 with a boiling point of $227^\circ C$. Unlike many other metals, Ru does have a volatile oxide, RuO_4 , which has a boiling point of $40^\circ C$ at atmospheric pressure. To etch Ru, it would then only be necessary to oxidize Ru into the tetroxide. In standard atmospheric conditions, Ru is oxidized by molecular oxygen and water to form a thin layer of native Ru dioxide, which is a stable solid, and further oxidation is unfavorable. While high temperatures ($>800^\circ C$) result in the formation of RuO_4 (Bell & Tagami, 1963), to enable etching of Ru in a manufacturing setting, it is necessary to use plasma. Unlike molecular oxygen, atomic oxygen is reactive enough to oxidize Ru and RuO_2 into RuO_4 as the reactions in Table 1.3. Like many other etching systems that have been developed, plasma processing provides the energy necessary to form reactive species like atoms and ions that can etch Ru.

Table 1.3. Oxidation reactions for Ru involving O₂ and O. The formation of RuO₄ is only favorable when atomic O is the oxidant.

Reaction	ΔG_{rxn} (eV)
$\text{Ru}_{(s)} + \text{O}_{2(g)} \rightarrow \text{RuO}_{2(s)}$	-2.6
$\text{RuO}_{2(s)} + \text{O}_{2(g)} \rightarrow \text{RuO}_{4(g)}$	1.0
$\text{Ru}_{(s)} + 2\text{O}_{(g)} \rightarrow \text{RuO}_{2(s)}$	-7.4
$\text{RuO}_{2(s)} + 2\text{O}_{(g)} \rightarrow \text{RuO}_{4(g)}$	-3.7

O₂ plasma etching of Ru is believed to proceed by first forming a layer of RuO₂ on the surface. Ru in this topmost layer is then further oxidized by O radicals to RuO₃ and RuO₄, which then desorb (Imai et al., 2023). Hsu, Coburn, and Graves measured chamber wall redeposition of Ru in O₂/Ar plasma and found that 75% – 99% of Ru and RuO₂ are redeposited onto the chamber walls, while no RuO₄ was detected in the foreline using FTIR. Ion mass spectrometry found that Ru⁺, RuO⁺, RuO₂⁺, and RuO₃⁺ were the most common Ru-containing ions in the plasma, while only small amounts of RuO₄⁺ were detected (Hsu et al., 2006).

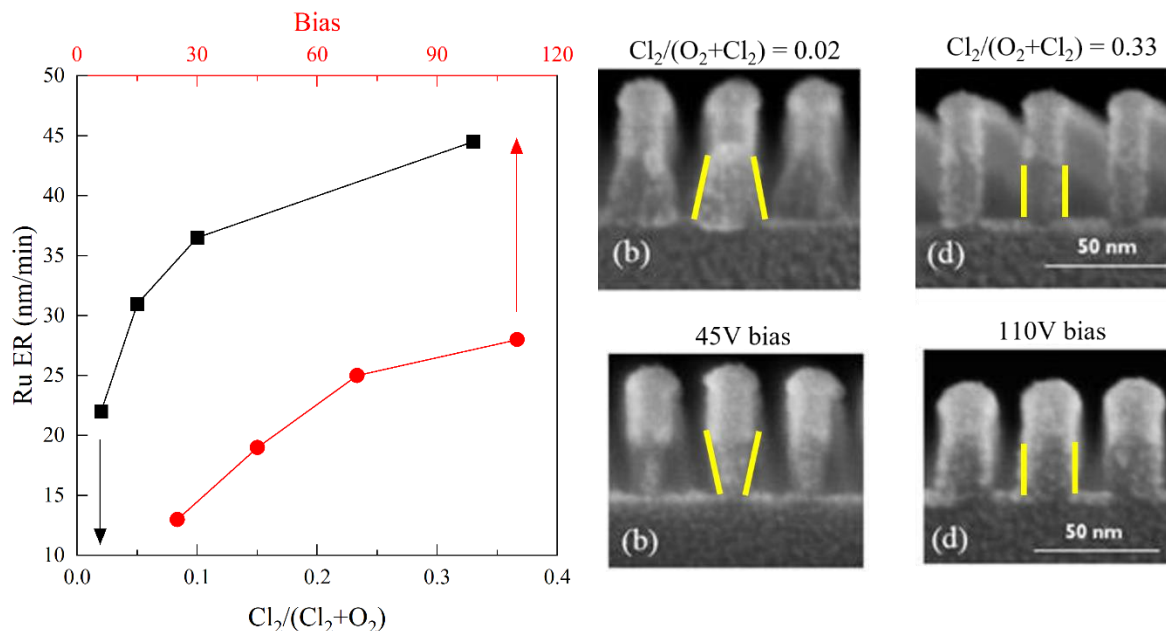


Figure 1.13. O_2/Cl_2 plasma etch of SiO_2 -patterned Ru from (Paolillo et al., 2018).

The addition of Cl_2 to the gas mixture is common in RIE of Ru and enhances the etch rate by both increasing the O radical density and lowering the energy required for the formation of RuO_4 and RuO_xCl_y species on the surface (Hsu et al., 2006; Imai et al., 2023; Paolillo et al., 2018). While Cl_2 addition enhances the etch rate, if the proportion of Cl_2 to O_2 is too high, non-volatile and etch-blocking RuCl_x species form, reducing the etch rate and increasing roughness through micro-masking effects (Matsui et al., 2024). Another common addition to gas mixture is Ar. While Ar does not contribute to the reactive etching of Ru, like Cl_2 it can affect the formation of O radicals through changes to the electron temperature and density, and does contribute to physical sputtering by ions. In mixtures of Ar and O_2 , the etch varied between chemical-dominated at high O_2 to Ar ratio and physical sputtering-dominated at low O_2 to Ar ratio. Other gases such as CF_4 and N_2 have also been shown to increase the O radical density and therefore the etch rate (Eung-Jik Lee et al.,

1998). With the exception of Cl_2 , the addition of other gases to the feed is not effective above 10% as further addition results in the dilution of the oxygen species that contribute chemically.

While the RIE of Ru using O_2 plasma with 10% Cl_2 has been optimized to enable anisotropic etching, the process conditions still represent a tradeoff between anisotropy and selectivity. The formation of less volatile chlorides on the sidewall may decrease the lateral etch rate, while increased bias increases ion energy and in turn the vertical etch rate, but it comes at a cost of increased damage to the hard mask and the introduction of chlorine to the surface (Matsui et al., 2024). As the hard mask is physically sputtered, it can redeposit on the sidewall, affecting features' critical dimensions as redeposition and oxidation occur on the hard mask's sidewall, causing it to expand laterally (Decoster et al., 2022). While minimization of the hard mask etch can be done by adjusting the bias duty cycle, resulting in cycles where ion bombardment is alternatively enhanced or reduced, this lowers the anisotropy of the process as vertical etch rate is reduced while lateral etching by radicals can still occur during the bias off time.

Beyond the complete etching of Ru trenches, alternate integration schemes are being developed that require the partial etching of Ru. Among these are the “topvia” and “self-aligned via” designs. One challenge in the fabrication of multiple layers of interconnects is the placement of vias, as slight offset of the pattern during lithography can lead to misalignment of the via and the previous layer, reducing the distance between lines, which increases capacitance delay and can even cause shorting. To alleviate this, in the topvia scheme shown in Figure 1.14a-c, a thicker Ru film is etched to form the lines, then those lines are partially etched while the vias are masked. Since the vias are formed from the lines, no edge placement error is possible. In the self-aligned vias process shown in Figure 1.14e, lines are recessed by a gentle etching process, which cause

any edge placement error during the via lithography to have less effect on the distance between lines.

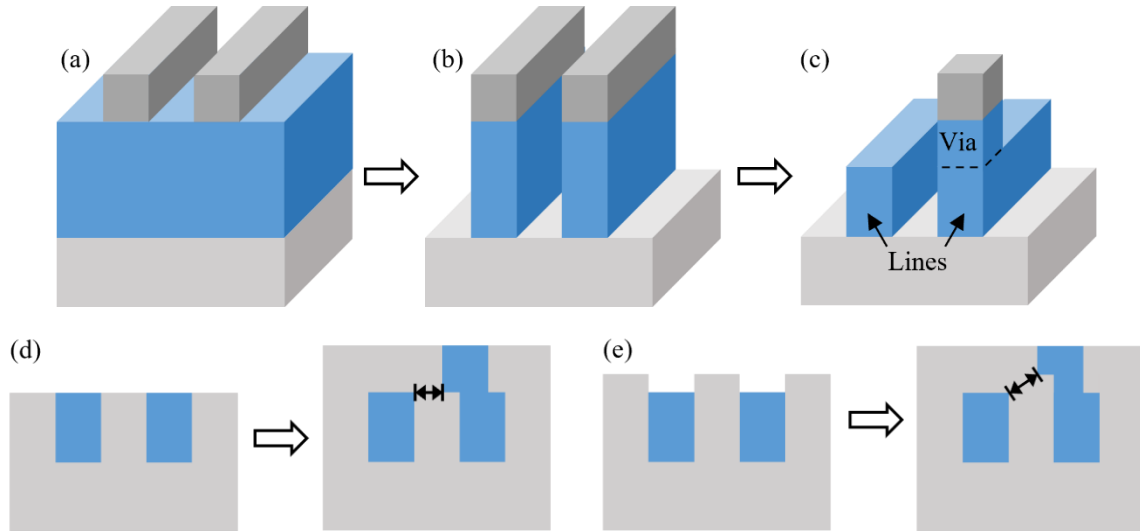


Figure 1.14. Schematics of partial Ru etching schemes for via alignment. (a) Hard mask is patterned for Ru lines. (b) Ru lines are etched. (c) Ru partial etching creates via and line structures. (d) Edge placement error in conventional Ru semi-damascene process. (e) Edge placement error is minimized by recessing of Ru lines.

In literature, there are very few processes that report a selectivity of Ru to hard mask materials such as TiN or SiO₂ greater than 10. Additionally, many are optimized for high etch rates by the addition of Cl₂ and large bias power. A review of Ru etch rates and selectivity to hard mask materials are listed in Table A.1. This presents a gap in etching capability for processes that require a high selectivity but are controllable with a low roughness and a purely vertical etch. All of these properties are highly desirable and necessary to enable the small scale and processing demands of current and next generation interconnect designs.

1.4 Surface Modification of Ru

From the previous sections, it is clear that the key to a successful subtractive etching process is selectivity, both with respect to material and surface orientation. While Ru is etched by plasma oxidation, a process that does not etch other relevant materials, it lacks anisotropy due to the reaction of O radicals with the sidewall. To induce anisotropy while avoiding loss of selectivity, plasma ALE can be used as a basis. Plasma is necessary to induce anisotropy through the directional bombardment of ions, and the formation of modification layers is necessary to create a difference in selectivity, but as in plasma ALE, only one step needs to be anisotropic to render the whole process anisotropic. The combination of multiple plasma steps that alternatively provide passivation and etching has long been utilized in the Bosch process for etching of high aspect ratio (>1000) holes into Si. There, alternating polymer deposition (passivation) and RIE are used. The polymer resists chemical etching but can be removed by ion bombardment. During the RIE step, the polymer is only removed at the bottom of the trench, exposing fresh Si to be etched by the RIE. This process of passivation, anisotropic removal of passivation, and etching can be adapted at a smaller scale for Ru. Avoiding the use of halogens, nitridation is an additional surface modification process that can be used to introduce a modified layer. Many nitrides are used as a coating for their resistance to corrosion and oxidation, so Ru nitride could act as a passivation layer during plasma oxidation of Ru. Using O₂ plasma to etch Ru, there must be a process that can remove RuN anisotropically. This would leave passivation on the sidewall, protecting it from etching by O radicals. Hydrogen is a good reductant, and is used in processes such as forming gas annealing to remove oxides. Similarly, it should be possible to use to remove nitrides and oxides from Ru. Since passivation by nitridation and etching by oxidation are expected to be isotropic processes,

anisotropy must come from the nitride removal step. This makes hydrogen plasma a strong candidate to remove passivation from the bottom of the trench, allowing oxidative etching vertically.

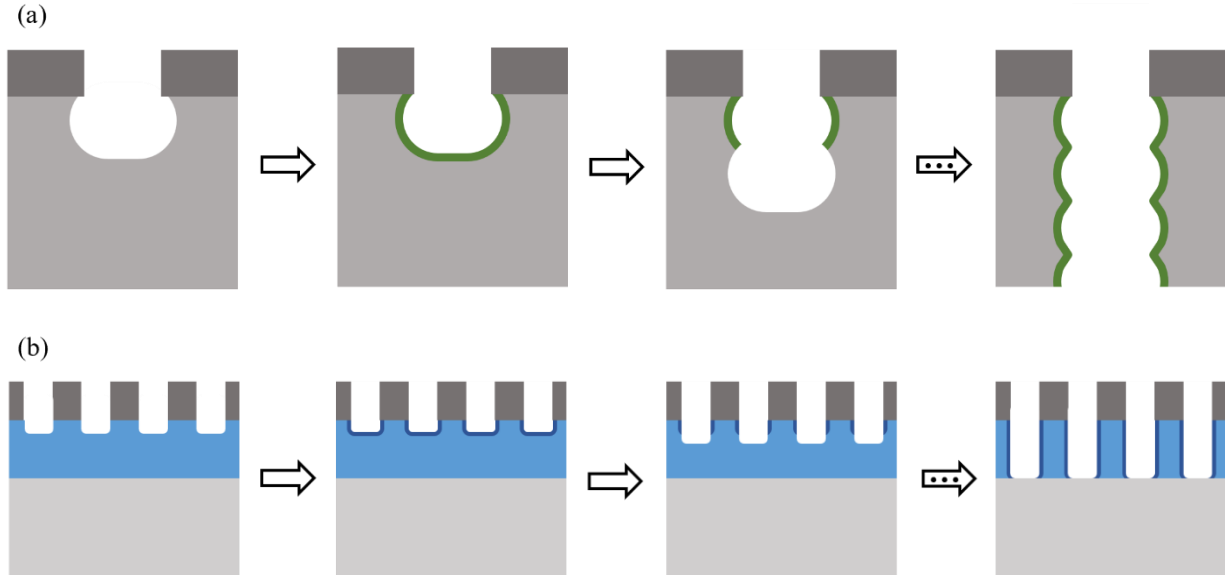


Figure 1.15. (a) Simplified diagram of the Bosch process, where deposition of a fluorocarbon passivation layer is used to protect the sidewall against isotropic etching by F radicals. (b) Diagram of proposed Ru etching process, where plasma nitridation forms a passivating layer that is removed by anisotropic reduction by H_2 plasma, allowing oxidative etching. Both processes utilize passivation and subsequent selective removal of the passivating layer from the bottom of the trench.

Nitridation has been utilized to form a protective layer for many materials due to the hardness and stability of many nitrides. Since N_2 itself is generally nonreactive, and some metal nitrides are metastable, with a positive free energy of formation, plasma nitridation in particular is a common method for formation of thin nitride films. It has been used to form nitrides as a protective layer on steel surfaces, a surface modification step in atomic layer etching of Ni, and on Si (Flis, 2010; Rauf et al., 2005; Smith et al., 2024). In the study of silicon nitridation, N radicals react with the surface, forming thin layers of the nitride, while ions penetrate deeper into the film

to form a thicker nitride layer (Seino et al., 2002). While plasma based nitridation of Ru has not been reported, the deposition of bulk RuN has been achieved with methods including pulsed laser ablation and sputtering using N₂ gas as a reactant (Cattaruzza et al., 2016; Kazari et al., 2022; Moreno-Armenta et al., 2007). In all cases, RuN formed with a 1:1 stoichiometry in the rock-salt or zincblende crystal structure. The zincblende structure is predicted to be the most stable form, but as a metastable compound all forms of RuN are shown to have positive free energies of formation. Since RuN has already been shown to form through deposition in a N₂ plasma-based environment, as in reactive sputtering, the plasma nitridation of Ru thin films should be a viable method for surface modification.

Hydrogen plasma has been used to treat Ru surfaces, as Ru is used as the protective capping layer in EUV lithography optics, where the removal of tin residues and oxidation of the Ru are both critical to maintain efficiency. It has also been used during hybrid deposition and etching schemes for Ru, where it is used after plasma oxidation is used as an etch back to remove any remaining oxide from the surface to maintain the quality of the film before further deposition. While Ru hydrides have only been studied in high pressure conditions as a method for hydrogen storage, as such a small particle, H may diffuse into Ru during plasma exposure. These results indicate the reduction of RuN is also possible with plasma.

To confirm, a thermochemical analysis of reactions with Ru and the three plasmas, N₂, H₂, and O₂ was performed to confirm the basic validity of the proposed process. Table 1.4 shows the formation of RuN by N₂ plasma and reduction of RuN by H₂ plasma were found to be favorable, while the oxidation of RuN was found to be less favorable than Ru, suggesting that RuN can be formed by plasma nitridation and passivate against etching in O₂ plasma. While ions enhance both

the nitridation and reduction processes, RuN is still formed during plasma nitridation without nitrogen ions, but is not fully reduced during reduction in H₂ plasma without hydrogen ions. The ion-driven passivation and reduction of RuN enables the etching anisotropy during the O₂ plasma step.

Table 1.4. Thermochemical reactions involving Ru and atomic N, H, and O.

Reaction	ΔG_r° (eV)
$\text{Ru}_{(s)} + 0.5\text{N}_{2(g)} \leftrightarrow \text{RuN}_{(s)}$	0.3
$\text{Ru}_{(s)} + \text{N}_{(g)} \leftrightarrow \text{RuN}_{(s)}$	-4.4
$\text{RuN}_{(s)} + 3\text{H}_{(g)} \leftrightarrow \text{Ru}_{(s)} + \text{NH}_{3(g)}$	-7.2
$\text{RuO}_{2(s)} + 4\text{H}_{(g)} \leftrightarrow \text{Ru}_{(s)} + 2\text{H}_2\text{O}_{(g)}$	-10.5
$\text{Ru}_{(s)} + 2\text{O}_{(g)} \leftrightarrow \text{RuO}_{2(s)}$	-7.4
$\text{RuO}_{2(s)} + 2\text{O}_{(g)} \leftrightarrow \text{RuO}_{4(g)}$	-3.7
$\text{RuN}_{(s)} + 2\text{O}_{(g)} \leftrightarrow \text{RuO}_{2(s)} + \text{N}_{(g)}$	-2.9

1.5 Atomic Layer Etching of CoFeB through Oxidation and Ligand Exchange

As the demand for scaling continues, improvements to material properties have become an important method for continued advancements. With increasingly specific requirements, the industry has turned to metal alloys that improve upon the performance of elemental metals. Simultaneously, reduced dimensions require etching processes that can be controlled to carefully remove a material without damage to the surroundings or substrate that a more brute-force method involving physical bombardment would do. Atomic layer etching provides an answer for both. Due to the self-limiting nature of each half-step in an ALE process, the process can be tuned to

select for chemistries that do not etch other materials, resulting in arbitrarily high selectivity. This also allows for a framework to be developed for the etching of many different metals and alloys.

Generally, the modification step consists of forming oxides, nitrides, halides, or organic ligands that saturate the surface. While continuous etching processes desire a product that is volatile, in ALE this modification layer need not be volatile as its purpose is to leverage selectivity during the actual etching step. The etchant during the second half of the cycle must selectively remove the modified layer over the base layer. While plasmas are normally a good choice for driving chemical reactions, the presence of ions and increased reactivity of radicals may in fact lower the selectivity. While differences in the volatility and bond energy of the modified and base layer may be exploited to allow ion-induced etching that is selective, an alternative approach is to use thermal processing, where reactant gases are introduced at an elevated temperature that promotes the etching reaction. In both cases, there is an ALE window moderated by temperature or ion energy, where below a threshold, the modification layer is not completely etched, and above which, the base layer begins to etch as temperature or ion energy increases.

In reality, ALE processes may not be completely self-limiting if the selectivity of the etching process is not infinite, etching occurs during the modification step, or the formation of the modification layer is not fully self-limiting, even in the optimal process window. Nevertheless, ALE processes give much more control over the etch than more traditional and aggressive RIE or wet etches do. Because of the alternating chemistries, selectivity vs. other materials is often higher, and the much lower etch rate can be critical for applications where very thin layers are being etched, or only partial etching is required. The surface-limited nature of ALE also results in the natural smoothening of the surface over the course of many cycles. One such case is in the

formation of uniform and conformal thin films. With deposition, there is a critical thickness, below which nucleation is not complete, and the film does not have complete coverage. Instead, a thicker and therefore uniform layer can be deposited, then etched back by ALE to the desired thinness.

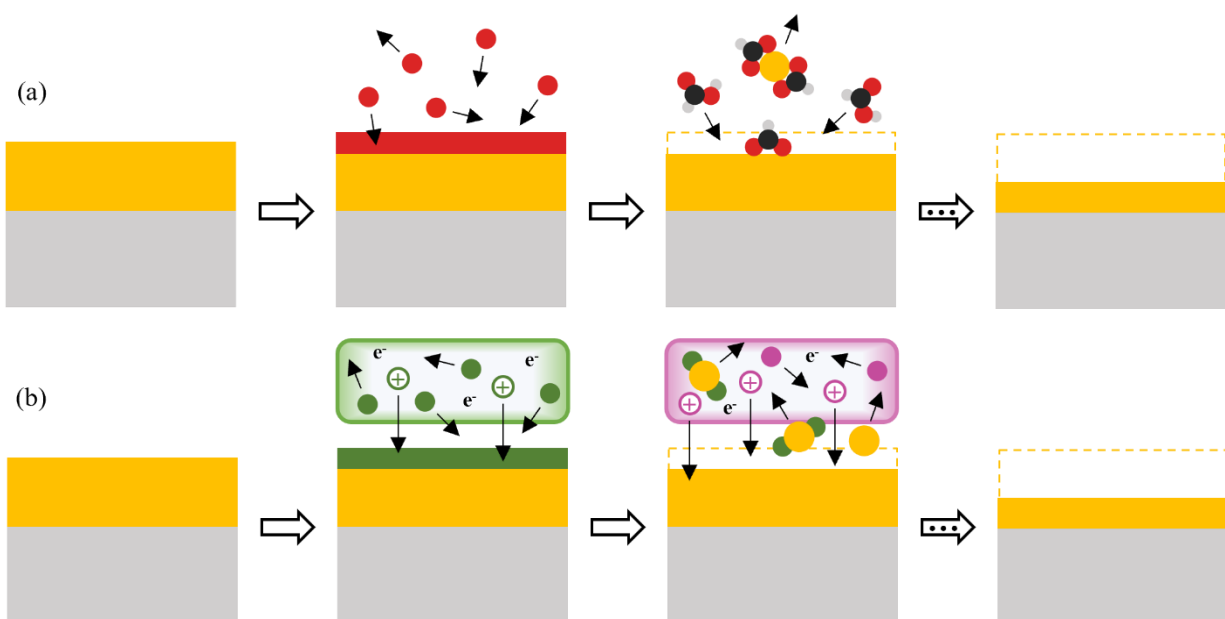


Figure 1.16. (a) Diagram of thermal ALE process. A modification layer is induced by oxidation, halogenation, or nitridation, followed by etching through ligand exchange. (b) Diagram of plasma ALE process. Exposure to reactive plasma species forms a modification layer that is removed by subsequent ion bombardment.

Two major types of ALE can be delineated based on the driving force of reactions, plasma and thermal. In plasma ALE, both steps occur in a plasma, increasing the reactivity of modifying species through the formation of radicals and ions. The modification species is often Cl, as it often forms compounds that are volatile enough to be removed by sputter deposition but do not spontaneously etch by themselves. Then, this modified layer can be sputtered by ions, most commonly Ar due to its chemical inertness. Since ions are used as the etchant, the process has

anisotropy, similar to the case of RIE, but the selectivity of the process to surrounding materials is limited, depending on the sputtering yields and thresholds of the various materials.

In thermal ALE, multiple types of processes can be applied to form the modification layer. The substrate, often a metal is modified from its base metal form to a higher oxidation state, commonly in the form of an oxide, halide, or nitride. To form a volatile etch product, ligand exchange is used to convert the oxidized layer, while the base metal layer is unaffected. A wide variety of etchants, often analogous to atomic layer deposition precursors due to the shared need for volatility and reactivity, can be used, but among the more common are organic ligands, including formic acid, and diketonates such as acetylacetone. Another process involves the substitution of the initial oxide with the oxide of another metal, which can then be removed with a standard etchant. Because thermal ALE is a purely chemical process, and reactants have no inherent directionality, it is isotropic.

An additional approach is a hybrid between plasma and thermal ALE. In thermal ALE, the modification step often involves oxidation or halogenation of a pure substance. In a hybrid process, this can be substituted with an equivalent modification step in a plasma, increasing the reactivity and inducing anisotropy, which is otherwise impossible in a thermal ALE process. By using a thermal-based etching step, the hybrid process avoids potential damage caused by sputtering.

A plasma-thermal ALE process used successfully to etch metals is plasma oxidation followed by removal by forming volatile metal diketonates, which has been demonstrated on metals such as Co, Cu, Ni, and Pt. However, this technique is difficult to extend to Ru as it is spontaneously etched by the initial plasma oxidation step. In its place, a technique that uses UV light to excite O₂ gas, oxidizing but not etching the Ru, has been developed to demonstrate ALE

of Ru (Coffey et al., 2021). Oxygen radicals have also been used as the oxidant, though as Table 1.3 and this work show, O radicals do spontaneously etch Ru, though at rates low enough that under the correct conditions they can still be used to modify the Ru surface. Ru fluorides are not very volatile, so fluorination has also been used as a modification step, followed by Ar ion bombardment.

As a whole, ALE approaches to the subtractive Ru etch provide an alternative to conventional RIE of Ru, but fail to provide both anisotropy and selectivity sufficient to meet the requirements. Thermal ALE provides selectivity, using oxidation and organic ligand exchange that avoid introducing halogens and do not etch Si-based dielectrics or hard mask, but with purely chemical etching mechanisms, are not anisotropic. Plasma or ion beam-based ALE can provide anisotropy, but the use of halogens such as fluorine and ion bombardment can damage the porous and easily-damaged SiCOH dielectrics in use at the back-end-of-line.

However, the etching of CoFeB in MTJ stacks is a much better candidate for ALE. Because the ALE of Co and Fe has been demonstrated, those processes can serve as a basis for developing ALE of CoFeB (Konh et al., 2019; Konh et al., 2021). Since the two steps are self-limiting, all of the modified layer can be removed, preventing the CoFeB from contamination and resulting degradation. Like Ni and Cu, Co and Fe have been shown to etch by organic acids, primarily β -diketonates such as acetylacetone (acac) and hexafluoroacetylacetone (hfac). Because of the varying affinity between Co, Fe, acac, and hfac, one concern is if one metal is preferentially removed, as has been hypothesized (Altieri et al., 2019). However, ALE of CoFeB has been demonstrated by chlorination followed by removal with acac (Konh et al., 2022).

Table 1.5. Boiling points of potential β -diketonate products. As the degree of fluorination increases, the products become more volatile. Data from (Fahlman & Barron, 2000).

Species	Molecular Structure	T _{boil/subl} (°C)
Co(acac) ₂	Co(C ₅ H ₇ O ₂) ₂	181
Co(acac) ₃	Co(C ₅ H ₇ O ₂) ₃	170
Co(tfac) ₃	Co(C ₅ H ₄ F ₃ O ₂) ₃	131
Co(hfac) ₃	Co(C ₅ HF ₆ O ₂) ₃	90
Fe(acac) ₃	Fe(C ₅ H ₇ O ₂) ₃	161
Fe(tfac) ₃	Fe(C ₅ H ₄ F ₃ O ₂) ₃	121
Fe(hfac) ₃	Fe(C ₅ HF ₆ O ₂) ₃	81

To formulate an ALE process that is able to remove CoFeB without halogenation or preferential etching, it is necessary to use oxidation in combination with formic acid, acac, and hfac. By utilizing multiple organic compounds, any preferential etching can be eliminated though the use of supercycles where organic acids that preferentially remove Co or Fe are alternated to result in a process with no net preference for either metal. The volatility of some potential products in Table 1.5, along with a preliminary thermochemical assessment of etching processes is shown in Table 1.6 for Co and Table 1.7 for Fe.

Table 1.6. Free energy of reactions involving Co and Co oxides with formic acid (FA), acetylacetone (acac), and hexafluoroacetylacetone (hfac). Due to limited literature data, reactions involving formic acid are in solution phase only.

Reaction	ΔG_r° (eV)
$\text{Co} + 2\text{FA}_{(\text{l})} \rightarrow \text{Co}(\text{FA})_{2(\text{a})} + \text{H}_{2(\text{g})}$	-0.52
$\text{Co} + 2\text{acac}_{(\text{g})} \rightarrow \text{Co}(\text{acac})_{2(\text{s})} + \text{H}_{2(\text{g})}$	0.06
$\text{Co}(\text{acac})_{2(\text{s})} \rightarrow \text{Co}(\text{acac})_{2(\text{g})}$	0.25
$\text{Co} + 3\text{acac}_{(\text{g})} \rightarrow \text{Co}(\text{acac})_{3(\text{s})} + 1.5\text{H}_{2(\text{g})}$	0.79
$\text{Co}(\text{acac})_{3(\text{s})} \rightarrow \text{Co}(\text{acac})_{3(\text{g})}$	0.04
$\text{Co} + 2\text{hfac}_{(\text{g})} \rightarrow \text{Co}(\text{hfac})_{2(\text{s})} + \text{H}_{2(\text{g})}$	-7.76
$\text{Co}(\text{hfac})_{2(\text{s})} \rightarrow \text{Co}(\text{hfac})_{2(\text{g})}$	0.16
$\text{CoO} + 2\text{FA}_{(\text{l})} \rightarrow \text{Co}(\text{FA})_{2(\text{a})} + \text{H}_2\text{O}_{(\text{l})}$	-0.76
$\text{Co}_3\text{O}_4 + 6\text{FA}_{(\text{l})} \rightarrow 3\text{Co}(\text{FA})_{2(\text{a})} + 3\text{H}_2\text{O}_{(\text{l})} + \text{O}_{2(\text{g})}$	-0.69
$\text{CoO} + 2\text{acac}_{(\text{g})} \rightarrow \text{Co}(\text{acac})_{2(\text{s})} + \text{H}_2\text{O}_{(\text{g})}$	-0.09
$\text{Co}_3\text{O}_4 + 6\text{acac}_{(\text{g})} \rightarrow 3\text{Co}(\text{acac})_{2(\text{s})} + 3\text{H}_2\text{O}_{(\text{g})} + \text{O}_{2(\text{g})}$	1.31
$\text{CoO} + 3\text{acac}_{(\text{g})} \rightarrow \text{Co}(\text{acac})_{3(\text{s})} + \text{H}_2\text{O}_{(\text{g})} + \frac{1}{2}\text{H}_{2(\text{g})}$	0.64
$\text{Co}_3\text{O}_4 + 9\text{acac}_{(\text{g})} \rightarrow 3\text{Co}(\text{acac})_{3(\text{s})} + 4\text{H}_2\text{O}_{(\text{g})} + \frac{1}{2}\text{H}_{2(\text{g})}$	3.51
$\text{CoO} + 2\text{hfac}_{(\text{g})} \rightarrow \text{Co}(\text{hfac})_{2(\text{s})} + \text{H}_2\text{O}_{(\text{g})}$	-7.91
$\text{Co}_3\text{O}_4 + 6\text{hfac}_{(\text{g})} \rightarrow 3\text{Co}(\text{hfac})_{2(\text{s})} + 3\text{H}_2\text{O}_{(\text{g})} + \text{O}_{2(\text{g})}$	-22.13

An additional challenge in oxidation of CoFeB is the formation of mixed oxidation state Co_3O_4 . While CoO can form $\text{Co}(\text{Ligand})_2$ compounds, the mixture of Co (II) and Co (III) atoms requires reduction during the etching process, which may provide a barrier for the formation of etch products, and introduce competition between etching and decomposition reactions as the temperature is varied (Partridge et al., 2023). While plasma oxidation has sufficient reactivity to form Co_3O_4 , it is necessary to remove organic residues from the surface that would otherwise remain on the surface and prevent further etching (Smith et al., 2024).

Table 1.7. Free energy of reactions involving Fe and Fe oxides with formic acid (FA), acetylacetone (acac), and hexafluoroacetylacetone (hfac). Due to limited literature data, reactions involving formic acid are in solution phase only.

Reaction	ΔG_r° (eV)
$\text{Fe} + 2\text{FA}_{(\text{l})} \rightarrow \text{Fe}(\text{FA})_{2(\text{a})} + \text{H}_{2(\text{g})}$	0.88
$\text{Fe} + 3\text{FA}_{(\text{l})} \rightarrow \text{Fe}(\text{FA})_{3(\text{a})} + 1.5\text{H}_{2(\text{g})}$	0.04
$\text{Fe} + 3\text{acac}_{(\text{g})} \rightarrow \text{Fe}(\text{acac})_{3(\text{s})} + 1.5\text{H}_{2(\text{g})}$	-0.03
$\text{Fe}(\text{acac})_{3(\text{s})} \rightarrow \text{Fe}(\text{acac})_{3(\text{g})}$	0.19
$\text{Fe} + 3\text{hfac}_{(\text{g})} \rightarrow \text{Fe}(\text{hfac})_{3(\text{s})} + 1.5\text{H}_{2(\text{g})}$	-2.34
$\text{Fe}(\text{hfac})_{3(\text{s})} \rightarrow \text{Fe}(\text{hfac})_{3(\text{g})}$	0.00
$\text{Fe}_2\text{O}_3 + 4\text{FA}_{(\text{l})} \rightarrow 2\text{Fe}(\text{FA})_{2(\text{a})} + 2\text{H}_2\text{O}_{(\text{l})} + \frac{1}{2}\text{O}_{2(\text{g})}$	1.04
$\text{Fe}_3\text{O}_4 + 6\text{FA}_{(\text{l})} \rightarrow 3\text{Fe}(\text{FA})_{2(\text{a})} + 3\text{H}_2\text{O}_{(\text{l})} + \text{O}_{2(\text{g})}$	0.54
$\text{Fe}_2\text{O}_3 + 6\text{FA}_{(\text{l})} \rightarrow 2\text{Fe}(\text{FA})_{3(\text{a})} + 3\text{H}_2\text{O}_{(\text{l})}$	0.41
$\text{Fe}_3\text{O}_4 + 9\text{FA}_{(\text{l})} \rightarrow 3\text{Fe}(\text{FA})_{3(\text{a})} + 4\text{H}_2\text{O}_{(\text{l})} + \frac{1}{2}\text{H}_{2(\text{g})}$	0.83
$\text{Fe}_2\text{O}_3 + 6\text{acac}_{(\text{g})} \rightarrow 2\text{Fe}(\text{acac})_{3(\text{s})} + 3\text{H}_2\text{O}_{(\text{g})}$	1.28
$\text{Fe}_3\text{O}_4 + 9\text{acac}_{(\text{g})} \rightarrow 3\text{Fe}(\text{acac})_{3(\text{s})} + 4\text{H}_2\text{O}_{(\text{g})} + \frac{1}{2}\text{H}_{2(\text{g})}$	0.98
$\text{Fe}_2\text{O}_3 + 6\text{hfac}_{(\text{g})} \rightarrow 2\text{Fe}(\text{hfac})_{3(\text{s})} + 3\text{H}_2\text{O}_{(\text{g})}$	-3.61
$\text{Fe}_3\text{O}_4 + 9\text{hfac}_{(\text{g})} \rightarrow 3\text{Fe}(\text{hfac})_{3(\text{s})} + 4\text{H}_2\text{O}_{(\text{g})} + \frac{1}{2}\text{H}_{2(\text{g})}$	-6.65

1.6 Summary

As emerging candidates for novel technologies and patterning schemes, development of etch processes for Ru and CoFeB is necessary for their integration into devices. The use of plasma to generate reactive species that can be used to modify and etch surfaces can be used to create a cyclic etching process. By combining multiple steps into a single process, greater control over the etch results can be achieved. In the case of Ru, the use of the N_2 and H_2 plasma steps is proposed to control the formation of inhibiting RuN , which can be used to protect the sidewalls from lateral etching during O_2 plasma exposure, enabling anisotropy. In the case of CoFeB, the synergistic plasma oxidation and vapor-based etching steps enable each other to create an atomic layer etching process. The oxidation step modifies the surface into metal oxides, which react with the organic acid vapor to form volatile organometallic compounds. To confirm the effects of these processes,

a variety of characterization techniques were used to demonstrate etching while contributing to the understanding of the chemical state and reactions that occur on the surface of the metal films during each process.

Chapter 2. Experimental Setup

Etching of Ru and CoFeB was experimentally performed using a variety of samples and processing techniques. Plasma processing was performed using an inductively coupled plasma reactor supplying O₂, N₂, or H₂ plasma with varying power, pressure, and applied bias. Vapor phase processing was performed using a custom vapor delivery system able to expose samples to formic acid or hexafluoroacetylacetone. To quantify the results of these etching processes on both blanket and patterned films, characterization techniques included the electron imaging techniques of scanning and transmission electron microscopy, to compositional and structural techniques such as x-ray photoelectron spectroscopy and x-ray diffraction, as well as plasma diagnostics such as optical emission spectroscopy. These techniques were used to determine not just the etching characteristics, but the underlying surface chemistry driving the processes, enabling further understanding of the mechanisms themselves.

2.1 Sample Preparation

Samples used in this work primarily consisted of thin films which were then cleaved using a diamond scribe into pieces with dimensions on the order of 1 sq. cm. Blanket film samples were composed of a flat film deposited onto a blank Si wafer. Patterned samples were blanket film Ru samples that a hard mask had been deposited onto and subsequently etched into, leaving a pattern atop a uniform Ru film.

2.1.1 Blanket Film Ru Samples

Blanket film Ruthenium samples were deposited by physical vapor deposition (PVD) using a Denton Discovery 550 sputtering system. An Ar discharge was generated, and a DC voltage was

applied to a 99.95% Ru target to bombard the target with ions and cause the sputtered Ru to redeposit on the 4" (001) Si wafers used as a substrate. The system was first pumped to 5×10^{-6} Torr, then the sputtering process proceeded with the conditions listed in Table 2.1. In order to form RuO₂ and RuN, O₂ or N₂ gases, respectively, were added. These gases dissociated in the plasma and reacted with the Ru as it deposited to form oxide and nitride films without the need for a pre-existing target.

Table 2.1. Sputter deposition conditions of Ru-based thin films.

Dep. material	Target material	Gas flow (sccm)	Power (W)	Substrate bias (V)	Pressure (mTorr)	Time (min.)	Thickness (nm)
Ru	Ru	40 Ar	200	None	5	15	160
RuO ₂	Ru	20 Ar/5 O ₂	200	None	5	15	320
RuN	Ru	10 Ar/20 N ₂	200	None	5	15	160

To confirm that the reactively sputtered films consisted of stoichiometric RuO₂ or RuN, as-deposited films were characterized with XPS and XRD. As determined by XPS, the O:Ru ratio of the RuO₂ film was 2.24, slightly higher than the stoichiometric ratio. Additional oxygen may be present bonded to adventitious carbon present on the surface of the film. The only peaks present in the XRD of the RuO₂ were Si, indicating that the RuO₂ was largely amorphous. The RuN film was found to be nearly stoichiometric, with a N:Ru ratio of 0.90. In ambient conditions, native oxide is formed on the RuN surface, displacing N and slightly reducing the overall ratio. The only peak present in the XRD corresponding to RuN was the (111) peak, which corresponds to a lattice parameter of 4.52Å, consistent with literature results for RuN in a zincblende-like structure.

Additional blanket films samples were provided by Samsung and consisted of 34 nm of PVD Ru on 300 nm of CVD SiO₂ atop a 12" Si wafer, with 1 nm of TiN deposited as an adhesion layer between the Ru and SiO₂. Patterned Samples

2.1.2 Patterned Ru Samples

Ruthenium films with hard masks were used to determine the effects of processing on patterned films. Three sets of samples were prepared, with a schematic of each shown in Figure 2.1, and the complete set of dimensions listed in Table 2.2.

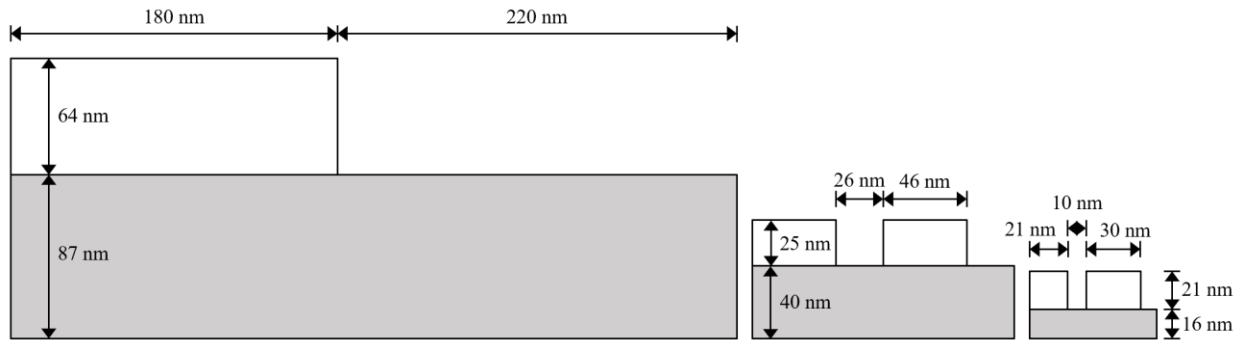


Figure 2.1. Schematics of patterned samples used in this work. All samples consisted of repeated line and space patterns with varying pitch and thickness.

Table 2.2. Dimensions of patterned Ru samples. (*) Line width alternates between the two listed values. Samples from set I were measured by SEM with a precision of 1 nm, while samples from sets II and III were measured by TEM with a precision of 0.1 nm.

Set	Pitch (nm)	WHM (nm)	$W_{opening}$ (nm)	t_{HM} (nm)	t_{Ru} (nm)	Trench AR
I	2008 ± 5	1008 ± 4	1000 ± 7	64 ± 2	87 ± 3	0.2
	1003 ± 2	492 ± 4	511 ± 4	64 ± 2	87 ± 3	0.3
	603 ± 2	281 ± 2	322 ± 3	64 ± 2	87 ± 3	0.5
	401 ± 5	181 ± 4	220 ± 6	64 ± 2	87 ± 3	0.7
II	72.1 ± 0.8	45.8 ± 0.8	26.3 ± 1.1	24.8 ± 0.7	40.8 ± 0.8	2.5
	42.4 ± 2.3	23.6 ± 6.6	18.8 ± 7.0	20.5 ± 1.2	40.8 ± 0.8	3.3
III	65.8 ± 1.0	$31.1 \pm 0.7 /$ $39.8 \pm 0.9^*$	30.3 ± 1.1	21.5 ± 0.9	16.4 ± 0.7	1.3
	34.9 ± 0.8	$13.6 \pm 0.8 /$ $28.3 \pm 0.7^*$	14.0 ± 1.0	19.2 ± 2.0	16.4 ± 0.7	2.5
	34.9 ± 0.4	$21.1 \pm 0.7 /$ $29.5 \pm 0.8^*$	9.5 ± 0.6	20.6 ± 0.7	16.4 ± 0.7	3.9

An initial set of patterned films was fabricated using an AJA ATC 2200-V sputtering system to deposit a 90 nm thick layer of Ru, then either 60 nm of SiO₂ or SiN_x, using a Si target and the addition of O₂ or N₂ gas, respectively. The conditions used for each material are listed in Table 2.3.

Table 2.3. Sputter deposition conditions of materials used to fabricate patterned samples.

Dep. material	Target material	Gas flow (sccm)	Power (W)	Substrate bias (V)	Pressure (mTorr)	Time (min.)	Thickness (nm)
Ru	Ru	45 Ar	200	None	3	10	90
SiO ₂	Si	25 Ar/2.5 O ₂	250	120	3	8.75	60
SiN _x	Si	25 Ar/2.5 N ₂	250	120	3	18.67	60

After deposition, a layer of anti-reflective coating, DUV-42P, was spun on at 2500 RPM for 30 seconds then baked at 220°C for 1 minute. The positive chemically-amplified photoresist UV6-0.7 was subsequently spun on at 3500 RPM for 30 seconds and baked at 135°C for 1 minute. The photoresist was patterned by an ASML DUV stepper with an exposure dose of 18 mJ. The pattern consisted of 12 mm by 12 mm squares split into quadrants of evenly spaced parallel lines with 400, 800, 1000, or 2000 nm pitches. After post-baking for 90 seconds at 135°C, the photoresist was developed by AZ300MIF develop for 80 seconds. The anti-reflection coating was then removed by O₂ plasma RIE with 100W RF bias and 10 mTorr pressure for 70 seconds. The hard mask SiO₂ and SiN_x were patterned by CF₄-based plasma with conditions in Table 2.4.

Table 2.4. Plasma etch conditions of hard mask materials.

Etch Material	Gas flow (sccm)	ICP power (W)	Substrate bias (W)	Pressure (mTorr)	Time (sec.)	Initial thickness (nm)
SiO ₂	35 CF ₄ /10 CHF ₃	800	50	3.8	30	65
SiN _x	50 CF ₄ /5 O ₂	500	50	3.8	30	65

The photoresist was stripped by an overnight acetone bath followed by isopropyl alcohol and DI water rinsing. The remaining residue was removed in a Tegal Plasmaline 515 asher with O₂ plasma at 200W power and 500 mTorr pressure for 5 minutes. Due to the gentle conditions relative to those used for Ru etching, this O₂ plasma did not result in the etching of Ru.

Patterned Ru films were provided by Samsung with pitches down to the tens of nanometers. The samples consisted of a SiO₂ hard mask on top of Ru samples prepared with the same specifications as the blanket Ru samples, but with Ru thickness varying from 16 to 40 nm. The complete list of sample dimensions is listed in Table 2.2.

2.1.3 Co, Fe, and CoFeB Samples

To investigate the etching of CoFeB, blanket film Co and Fe samples were deposited alongside CoFeB. The Co and Fe were deposited by e-beam evaporation in a CHA Solution system directly onto a 4" Si wafer, resulting in films with thicknesses of 38 and 33 nm, respectively. CoFeB was deposited by PVD in a Denton Discovery 550 sputtering system. First, 10 nm of Ti was deposited, then CoFeB was sputtered from a target with nominal composition of 20:60:20. Sputtering occurred using a DC source with a current of 0.2 A at a pressure of 20 mTorr with 40 sccm of Ar flowing in. The sputter time was set to 2 minutes or 10 minutes, resulting in two sets of samples with a CoFeB thickness of 12 nm or 60 nm, respectively. The as-deposited composition was determined to be 21.0:57.9:21.1 by XPS.

2.2 Sample Processing

The etching of both Ru and CoFeB samples was primarily carried out through exposure to plasma or vapor. Preliminary investigations into CoFeB were done in solution phase.

2.2.1 Inductively Coupled Plasma

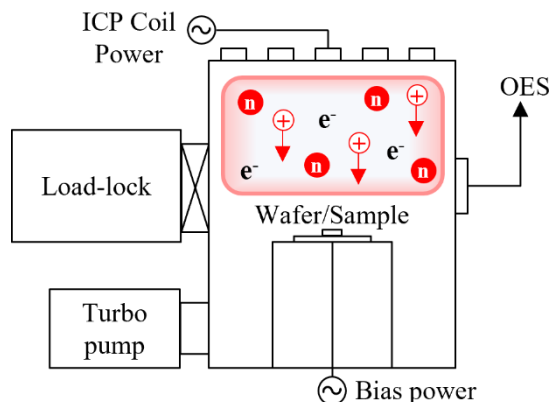


Figure 2.2. Schematic of the inductively coupled plasma reactor used in this work.

Plasma processing of samples was performed using a PlasmaTherm SLR 770 ICP as shown in Figure 2.2. The reactor uses an inductively-coupled plasma (ICP) generated by RF power at 2 MHz through a cylindrical coil at the top of the reactor. An additional RF power source running at 13.56 MHz was connected to the substrate, allowing for control over the bias. The process gases supplied to the chamber were Ar, O₂, H₂, and N₂, BCl₃, Cl₂, HBr, and CH₄, though only the first four listed were used in this work. The chamber was pumped by a turbo-molecular pump, and samples were inserted into the chamber through a load-lock chamber after adhesion to 4" (001) Si wafers using thermal paste.

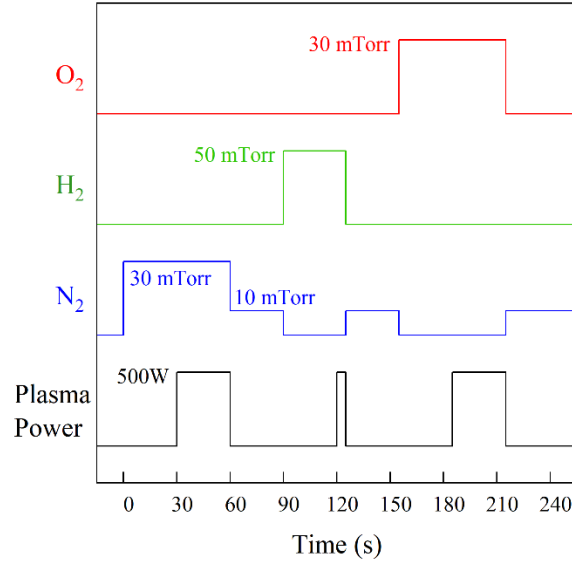


Figure 2.3. Diagram of the cyclic N₂/H₂/O₂ process. Each plasma step was preceded by 30 seconds of gas flowing in and followed by a 30 second purge step using N₂. The plasma on time was 30, 5 and 30 seconds for N₂, H₂, and O₂, respectively.

Prior to processing, a cleaning process was run in the empty chamber, using 5 minutes of O₂ plasma at 800W ICP power, 50W bias power, and 30 mTorr pressure. After the cleaning process, if N₂ or H₂ plasma process was to be used, it was first run with a blank Si wafer as a dummy run before the actual process was run. Each plasma exposure step was preceded by an initial step where the process gas was allowed to flow in and equilibrate for 30 seconds prior to ignition of the plasma. In cyclic processes, each step was followed by a 30 second N₂ purge at 10 mTorr, as is shown in Figure 2.3. The standard conditions used for N₂, H₂, and O₂ plasmas are listed in Table 2.5.

Table 2.5. Standard plasma conditions used in this work. Blanket film results used a H₂ plasma duration of 5 seconds, while patterned film results used either 5 or 15 second duration, as noted in the text.

Step	Gas flow (sccm)	Power (W)	Substrate bias (W)	Pressure (mTorr)	Time (sec.)
N ₂	30	500	10	30	30
H ₂	50	500	15	50	5/15
O ₂	30	500	None	30	30

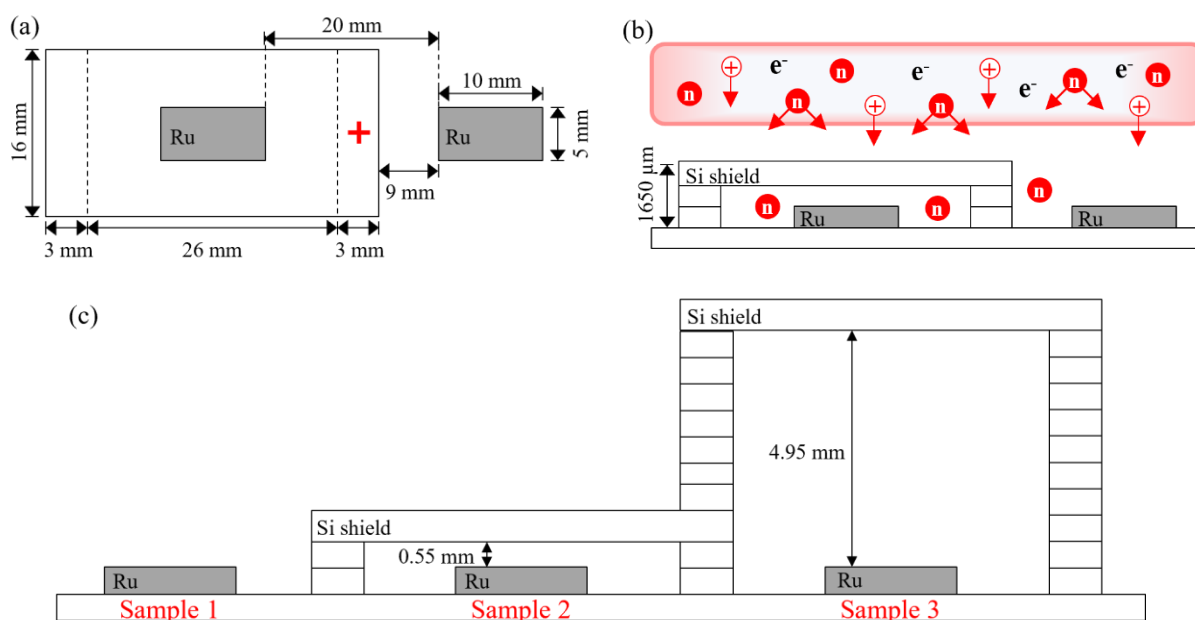


Figure 2.4. Schematics of samples used for ion blocking experiments. (a) Top-down view with dimensions labeled. (b) Side view illustrating that ions are unable to reach the left-hand sample, while the gap ensures that radicals can still reach the sample. The samples were placed equidistant from the center of the 4" Si carrier wafer. (c) Schematic of the three sample setup, with two samples placed under Si shields with varying height in order to determine the effect of shield dimensions.

To test the effects of plasma without ion bombardment, samples were placed below a Si wafer piece with an air gap as shown in Figure 2.4(a) and (b). This allowed radicals to reach the surface, but ions were blocked due to their directionality. Experiments with the ion shielding were

ran simultaneously with exposed samples, allowing the effect of the shielding to be directly compared.

To determine if the height of the Si shield had an effect on the radical flux, and therefore the results of plasma exposure beyond the removal of ions, three samples were exposed to O₂ plasma in parallel. Sample 1, shown schematically in Figure 2.4(c), was exposed to ions. Sample 2 was placed under the Si shield with a 0.55 mm gap, which was used in the other Si shielding experiments. Sample 3 was placed under a shield with 4.95 mm gap, larger than the mean free path, λ , of the neutrals species predicted using kinetic gas theory

$$\lambda = \frac{kT}{\sqrt{2}\pi d_k^2 P} \quad (2.1)$$

where T is the temperature and P the pressure of the gas, while d_k is the kinetic diameter of the gas, in this case 346 pm for O₂. At a pressure of 30 mTorr and ICP power of 500W, the neutral temperature has been measured to be roughly 630K in conditions similar to this work (Kiehlbauch & Graves, 2003), resulting in a mean free path of 4.1 mm. Since the height of the Si shield setup for sample 3 was too tall to be loaded through the loadlock, it was directly placed into the vented chamber for a single experiment. The etch rate of sample 2 and 3 were found to be 40% and 50%, respectively, of the etch rate of sample 1. This indicates that the shielding of ions is a more significant contributor than radical flux to the difference in results seen from shielded samples.

2.2.2 Vapor Delivery Chamber

To expose samples to organic vapor, a custom-built chamber shown schematically in Figure 2.5 was used. The etch chamber itself consisted of a 5-way junction, with connections to the chamber door, pump line, N₂ vent line, and vapor delivery line, in addition to a sample stage

with extendable bellows to allow it to be retracted into the chamber with a rack and pinion. The pressure was monitored with a Baratron capacitance manometer with a range from 0.05 – 1000 Torr. The pressure was maintained by a mechanical pump with an inline cold trap used to collect etch products. Heating the chamber was done with two sets of heating tape, each connected to a Variac voltage transformer that controls the heat output. One heating tape is wrapped around the etch chamber and connecting lines in order to heat the sample during vapor exposure and prevent deposition of product or reactant species on the sidewall during etching. The other tape is wrapped around the line from the vaporizer to the etch chamber to prevent condensation of the reactant. While both could be controlled independently, but were set to the same temperature as the vaporizer between 80 – 120°C.

After mounting a sample to the stage with copper tape and retracting it into the chamber, the mechanical pump was opened to the chamber to pump it down to its base pressure of < 10 mTorr. To deliver vapor to the chamber, the appropriate valves between either the formic acid or hfac ampoule were opened, and the ampoule was pressurized with a brief, 1 second pulse of N₂. The liquid is pushed through the system by this, so when the liquid flow controller (LFC) and mass flow controller (MFC) are opened, liquid reaches the vaporizer, and N₂ carries the vapor into the chamber.

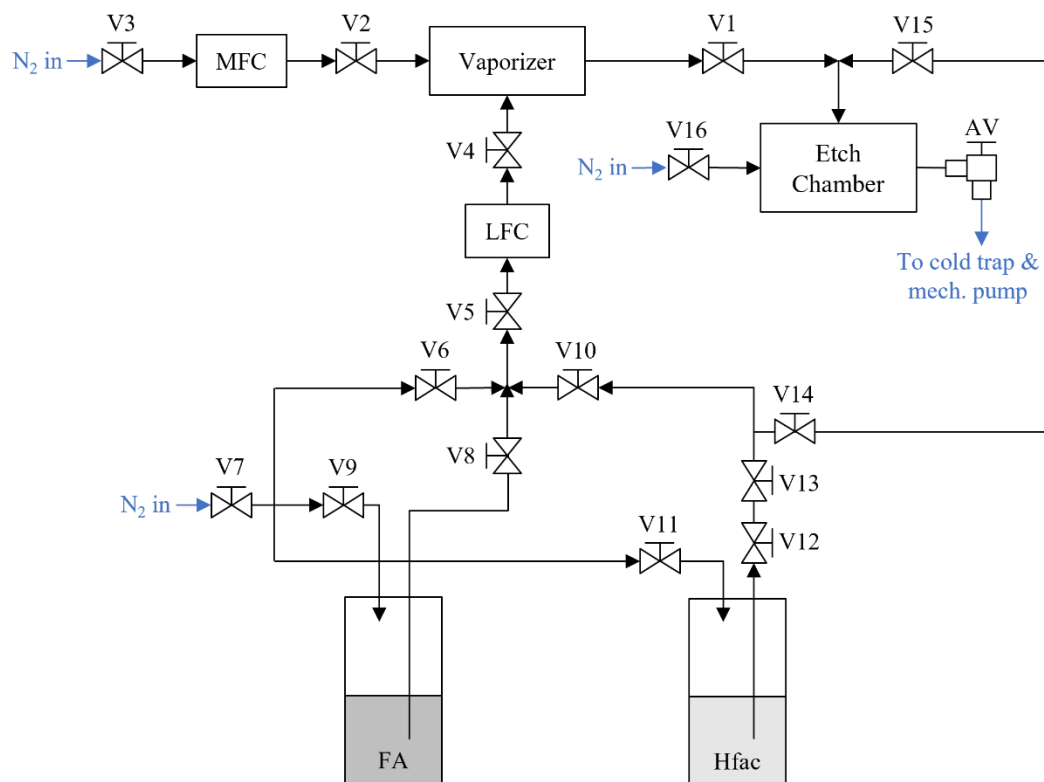


Figure 2.5. Schematic of the vapor chamber. Samples are placed on an extendable stage in the etch chamber. Formic acid or hfac ampoules are filled with liquid, then charged with N_2 to push liquid through the system into the vaporizer, where N_2 is used as a carrier to bring the vapor into the chamber.

Due to the use of N_2 as a carrier gas, the partial pressure of formic acid must be estimated from the overall pressure of the chamber. Figure 2.6 shows the pressure of the chamber with or without formic acid as N_2 is let into the chamber. At 350 Torr, the partial pressure of formic acid is 164 Torr. While the rate of rise of N_2 alone is nearly perfectly linear, there is some fluctuation in the flowrate of formic acid into the chamber, which may be due to air bubbles in the liquid delivery line and/or fluctuations in the temperature of the vaporizer as formic acid at room temperature reaches it and the heating controller adjusts to match.

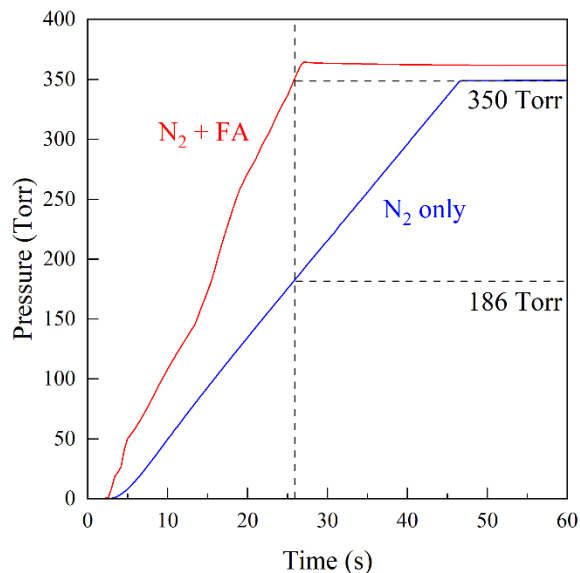


Figure 2.6. Rate of rise of pressure after opening the N₂ MFC and/or formic acid LFC. With formic acid entering the chamber, a pressure of 350 Torr is reached after 26 seconds. For an equivalent period of time with only N₂, the pressure reaches 186 indicating that the partial pressure of formic acid vapor in the chamber is 164 Torr.

2.2.3 Solution Phase

Solution phase etching of CoFeB films was carried out using primarily dilute aqueous solutions of formic acid (FA, Sigma-Aldrich, 95%) and acetylacetone (acac, Sigma-Aldrich, $\geq 99\%$). To dilute the solution to 1%, 10 mL of the organic acid was added to 90 mL of DI water, then gently agitated to form a 10% solution. Heating and stirring was required to dissolve the acac into water, while formic acid was readily soluble. Then, 10 mL of the 10% solution was added to 90 mL of DI water to form the 1% solution. On a hot plate, a DI water bath was heated to the desired temperature, then the solution was placed into the hot bath. This prevented the smaller amount of solution from overheating while maintaining an even temperature throughout. Samples were placed into the solution at a 90 degree angle to prevent them floating due to surface tension,

and removed the same way. After exposure to the solution, samples were washed in a room-temperature DI water bath for 1 minute, then dried with an air blower.

2.3 Plasma Diagnostics

2.3.1 Plasma Properties

The electron temperature and plasma density are two important characteristics that control the composition and resulting effects of a plasma discharge. However, these values cannot be obtained from the operating conditions directly, requiring a Langmuir probe to be used. The probe is immersed into the plasma, generating an I - V curve as the bias voltage applied to the probe, V_p , is swept through, as shown in Figure 2.7(a). When the probe is biased negatively relative to the plasma potential, V_s , positively charged ions are attracted to the probe, generating a current, while a positive bias results in electrons generating a current. Since the two species are oppositely charged, their currents cancel out at the floating potential, V_f , and by convention, the electron current is taken to be positive.

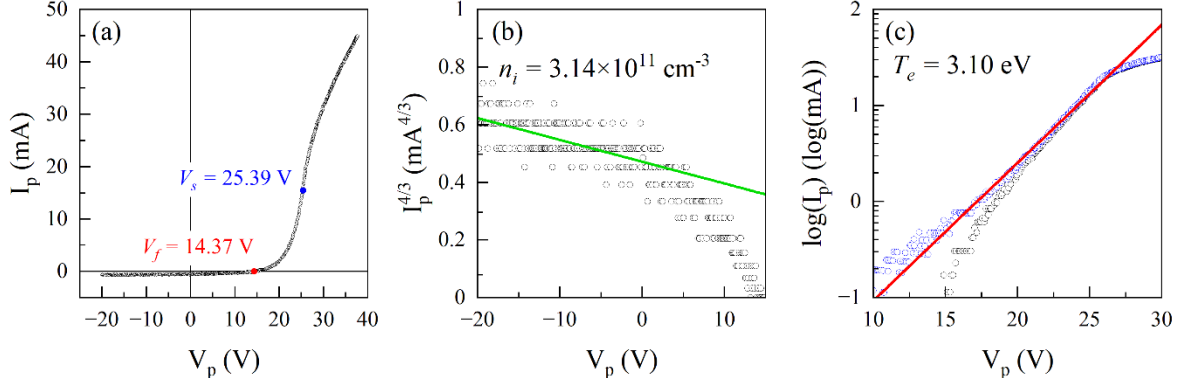


Figure 2.7. Langmuir probe data collected in N_2 plasma at 500W ICP source power and 35 mTorr. (a) Probe current as a function of probe potential. The floating potential, V_f , occurs at the point where ion and electron currents are equal, and the net current is zero. The plasma potential, V_s , can be found where the second differential of the I-V curve is equal to zero, or approximately the point where the electron current begins to saturate. (b) Ion saturation region of the I-V curve. The line fitted to the ion current (green) is plotted, and the resultant ion density, n_i , is listed. (c) Exponential region of the I-V curve, plotted on semi-log scale. After removing the ion current, the resulting data (blue) can be fit to a straight line (red). The reciprocal of the slope is equal to the electron temperature, kT_e .

To determine the electron temperature, it is necessary to model the behavior in the exponential region. This region occurs roughly between the floating potential and the plasma potential, where the electron current increases exponentially as such,

$$I_e = I_{e,sat} \exp\left(\frac{e(V_p - V_s)}{kT_e}\right), \quad I_{e,sat} = en_e A_p \left(\frac{kT_e}{2\pi m_e}\right)^{\frac{1}{2}} \quad (2.2)$$

where kT_e is the electron temperature in eV, A_p is the exposed probe surface area, and m_e is the mass of an electron (Chen, 2003). Above this region, the electron saturation current is reached. Ideally, the saturation current would be seen as a flat line in the probe current when the potential increases above V_s , but in practice the current continues to increase above the knee, particularly in RF plasmas. The plasma potential V_s can be more precisely determined by finding the maximum

slope of the I-V curve or equivalently where the second derivative, d^2I/dV^2 is zero. Since the total current measured by the probe is the sum of the electron current and ion current (each with opposing signs), the ion current can be subtracted to obtain the electron current. To obtain the electron temperature, the current can then be fit by a straight line on a $\log(I_p)$ -V plot. Rearranging equation 2.2 into the form of a straight line,

$$\ln(I_e) = \frac{e(V_p - V_s)}{kT_e} + \ln(I_{e,sat}) \quad (2.3)$$

it can be seen that the reciprocal of the slope of the straight line is kT_e , the electron temperature in eV. To find the ion current to carry out this analysis, it is necessary to examine the ion saturation region. While the ion current at the floating potential is the Bohm current,

$$I_B = \alpha_0 enA_p c_s, \quad \alpha_0 \equiv e^{-\frac{1}{2}}, \quad c_s \equiv \left(\frac{kT_e}{m_i}\right)^{\frac{1}{2}} \quad (2.4)$$

this value neglects effects such as sheath expansion that cause the ion current to vary with the probe bias. When $V_p \ll V_s$, the ion current dominates, and the data from this region can be used to fit to a model for ion collection. For cylindrical probe tips, such as the one used in this work, there are several theoretical approaches that have been developed to fit to the ion saturation current. Orbital-motion-limited (OML) theory assumes an infinite sheath radius and does not consider collisions or the existence of an absorption edge below which all ions are collected, and predicts $I^2 \propto V$ in the ion saturation region (Mott-Smith & Langmuir, 1926). Other theories exist, such as Allen-Boyd-Reynolds (ABR) (Allen et al., 1957), which solves for Poisson's equation assuming no orbital motion, and Bernstein-Rabinowitz-Laframboise (BRL) (Laframboise, 1966), which considers angular momentum of ions with a Maxwellian energy distribution. For RF plasmas with

density in the range of $10^{10} - 10^{12} \text{ cm}^{-3}$, the I - V curve in the ion saturation region has been found to best fit with $I^{4/3} \propto V$, as shown in Figure 2.7(b) (Chen et al., 2002). Using the fitted line, the ion current can be extrapolated beyond the ion saturation region and into the exponential region.

To determine the plasma density n , which for a quasi-neutral plasma is equal to the ion and electron density, it is necessary to use a model for ion collection in RF plasmas as described by Chen. Using the Child-Langmuir law, current density J is related to sheath thickness d and potential V ,

$$J = \frac{4}{9} \left(\frac{2e}{m_i} \right)^{\frac{1}{2}} \epsilon_0 V^{\frac{3}{2}} \frac{1}{d^2} \quad (2.5)$$

where m_i is the mass of an ion and ϵ_0 is the permittivity of free space. The equation can be rearranged in terms of d , and substituting in Bohm current density, $J_B = \frac{I_B}{A_s}$, and the Debye length, λ_D , results in

$$d = \frac{1}{3} \left(\frac{2}{\alpha_0} \right)^{\frac{1}{2}} (2\eta_f)^{\frac{3}{4}} \lambda_D, \quad \lambda_D \equiv \left(\frac{\epsilon_0 k T_e}{n e^2} \right)^{\frac{1}{2}}, \quad \eta_f = \frac{e(V_f - V_s)}{k T_e} \quad (2.6)$$

The Bohm current at the sheath edge can also be rearranged in terms of d , with the current equal to the contribution of ions at the floating potential

$$d = I_i(V_f) / (2\pi L_p \alpha_0 e n c_s) - R_p \quad (2.7)$$

Combining equations 2.6 and 2.7 and rearranging with respect to $n^{1/2}$, results in an equation that can be solved for $n^{1/2}$ using the quadratic formula

$$R_p (n^{1/2})^2 + \frac{1}{3} \left(\frac{2\epsilon_0 k T_e}{\alpha_0 e^2} \right)^{\frac{1}{2}} (2\eta_f)^{\frac{3}{4}} (n^{1/2}) - \frac{I_i(V_f)}{2\pi L_p \alpha_0 e c_s} = 0 \quad (2.8)$$

$$n = \left[\frac{-B + \sqrt{B^2 + 4AC}}{2A} \right]^2, \quad A = R_p, \quad B = \frac{1}{3} \left(\frac{2\epsilon_0 k T_e}{\alpha_0 e^2} \right)^{\frac{1}{2}} (2\eta_f)^{\frac{3}{4}}, \quad C = \frac{I_i(V_f)}{2\pi L_p \alpha_0 e c_s} \quad (2.9)$$

The value of the ion current at the floating potential can be found by extrapolating the fitted $I^{4/3}$ - V line to the value at V_f , while the electron temperature can be found as described above.

In this work, data was collected with a Hiden ESPion Langmuir probe. It was necessary to compensate for the fluctuations in V_s caused by the RF power source that would result in measurements of the probe current that did not reflect the actual parameters of the plasma. After collecting the raw I - V data, it was processed by a custom Python script based on the theory as described above. The value of V_s was found by finding the maximum of dI/dV . As the raw I - V data was noisy, a Savitsky-Golay filter with polynomial order of 2 and a window of 20 points was used to calculate the derivative. The value of V_f was found where the probe was zero. Since the current was measured with discrete values and some noise was present, there were often multiple points in the same region where the current was zero. In this case, the mean value of the probe potential at these points was taken as the value of V_f . An estimate of the electron temperature was used to determine the ion saturation and electron exponential regions,

$$kT_{e,est} = e(V_s - V_f)/4 \quad (2.10)$$

The ion saturation region was set between the minimum value of the probe potential and $V_f - 4kT_{e,est}/e$, while the exponential region was set between V_s and $V_s - 4kT_{e,est}/e$. The ion saturation region in $I^{4/3}$ - V scale is then fit with a straight line. Using this fit, the ion current is subtracted from the current to obtain the electron current for kT_e calculations, and the ion current at the floating potential is found for n_i calculations. In the exponential region, the electron current is reduced to log scale, then a straight line fit is applied to find kT_e as the reciprocal slope. Using

kT_e , the ion density (and therefore electron density) can be found using equation. Both straight line fits are performed using the NumPy library's polyfit function, which minimizes the least squares error to find the slope and intercept.

2.3.2 Optical Emission Spectroscopy

Optical Emission Spectroscopy (OES) uses light generated by excited species present in the plasma to determine its composition. The light detected by the technique ranges from the near ultraviolet (300 nm) to near infrared (1000 nm), allowing a variety of electronic transitions to be seen. In plasma, collisions of molecular and atomic species with free electrons can cause excitement of an electron to a higher energy level. As the excited electrons transition from a higher to lower energy state, they release the equivalent amount of energy as light, which falls in the visible range when the energy is within 1 – 4 eV. Since energy levels are characteristic to an element and ionization state, as well as to the vibrational and rotational energy of molecules, the peaks that appear in the optical emission spectrum of a plasma can be used to give a qualitative composition of the plasma.

As the energy of the light emitted is the difference between the higher and lower energy state, the position that it appears in does not necessarily correlate to the energy of the higher state. However, knowledge of the energy states of a species can be used to determine where intensity peaks should be. In atomic species, the energy levels of excited electrons can be described by the quantum numbers using a term symbol with the notation $^{2S+1}L_J$ where S is the total spin quantum number of the atom, L is the total orbital quantum number of the atom, and J is the total angular momentum quantum number, which is an integer between $L+S$ and $|L-S|$. Since the total spin and orbital angular momentum of completely filled orbital is zero, S is therefore equal to the sum of

spin magnetic quantum numbers, m_s , of electrons in unfilled orbitals, and L is equal to the sum of orbital magnetic quantum numbers in unfilled orbitals, m_l . The most significant contributions to the difference in energy levels arises from the principal, n , and orbital, l , quantum numbers that correspond to the electron shell and orbital that the electron resides in. The values of S and L also contribute to the differences in the energy levels on the order of a few eV, and the possible values of J lead to differences on the order of 1×10^{-4} eV, which is known as the fine structure. In this work, the spectrometer is unable to distinguish fine structure, with FWHM on the order of 0.1 to 1 nm, so the characteristic peaks correspond to variations in the value of L and S . In the case of molecular species, in addition to the electronic state, the energy level can vary based on excitations in the vibrational and rotational energy of the molecule, causing wide bands to appear corresponding to an individual electronic transition with many possible vibrational energy states. Example spectra are shown in Figure 2.8 with the most intense transitions labeled.

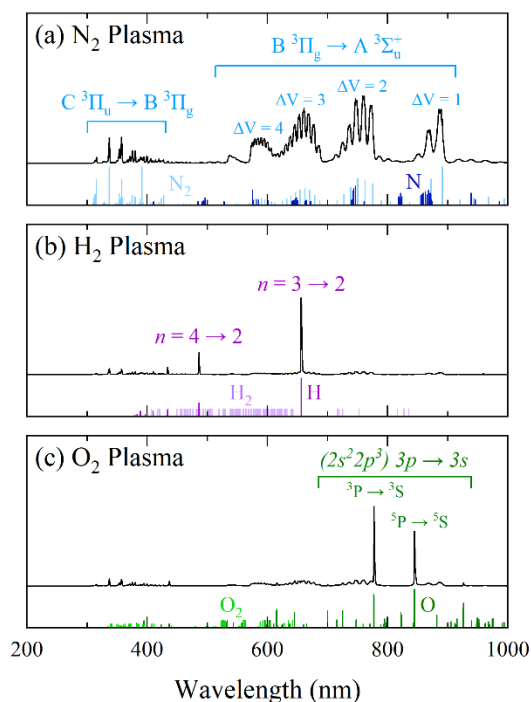


Figure 2.8. Optical emission spectra of (a) N₂ plasma. The molecular term symbols of the bands are shown along with the net difference in vibrational quantum number. (b) H₂ plasma. Transitions are given by the principal quantum number change, since the difference in energy between terms with differing l , m_s , m_l , and j is too small to be distinguishable. (c) O₂ plasma.

Since the distribution of electron energy in a plasma is condition dependent, the distribution of excited energy states and therefore optical emission lines also varies. This means that quantification of plasma composition must require additional information. Actinometry is a technique that uses trace amount of nonreactive gases, primarily noble gases such as Ar, to provide a basis for quantification. When a known amount of Ar is added to the gas (commonly 5%), the intensity of an Ar line with similar threshold energy and cross section compared to the intensity of a target species transition can be used to determine the ratio between the two species. Since the Ar concentration is known, this can be extrapolated to find the amount of the target species present.

2.4 Sample Characterization

To understand the initial state and effects of plasma exposure on Ru, it was necessary to use a variety of techniques to determine physical characteristics such as film thickness and crystal structure as well as chemical composition and bonding.

2.4.1 Etch Rate and Film Thickness

As one of the primary etching characteristics, the etch rate of a process must be well understood. By determining it, and how it reacts to changes in the process as well as on structures with varying aspect ratio and surfaces, the viability of a process can be demonstrated. An etch rate can be simply described as the decrease to film thickness versus exposure time, or number of cycles in the case of cyclic processes such as ALE. This requires a technique that can determine the film thickness. One common method is using spectroscopic ellipsometry, in which a spectrum of light is reflected off the sample, affecting its polarization, which can be measured in the form of two parameters, the amplitude ratio, Ψ , and phase shift, Δ . Based on material properties, a model predicting the two parameters can be constructed and used to fit a thickness value. While ellipsometry is well suited to measure transparent dielectric films, metal films have a large extinction coefficient and above thicknesses of 20-30 nm are too opaque to measure correctly.

Instead, an alternate method for determining thickness is to use microscopy. While optical microscopes do not have the resolution to measure films with thicknesses in the tens of nanometers, electron microscopy techniques can. Scanning electron microscopy (SEM) has nanometer-scale resolution, and while samples must be cleaved in order to measure their cross-section, is otherwise non-destructive. To generate an SEM image, an electron beam is focused on the sample through a series of electrostatic and electromagnetic lenses, then resultant electrons from the sample are

collected by a detector. Unlike conventional optical microscopy, the detector measures current, but does not have spatial resolution. Instead, the electron beam, which can be focused below a nanometer spot size, is moved across the sample using a scanning coil, forming a raster image. The electrons generated by the incident beam can be categorized as secondary electrons or backscattered electrons. Secondary electrons have energy below 50 eV and are generated from approximately up to 10-20 nm deep in the sample as electrons from the sample are ejected. This results in topographical contrast, as the increasing angle of incidence results in a larger beam spot, allowing more secondary electrons to reach the surface. Backscattered electrons are primary electrons that have collided within the sample, and are higher energy than secondary electrons, and have yield proportional to the atomic number of the target material. This is termed Z contrast, as different materials appear at different brightness, allowing for improved material characterization. Due to the greater depth that backscattered electrons can reach, the size of the region affected by the incident beam is greater, and the resultant resolution is lower. X-rays are also generated by the incident beam with characteristic energy to the target elements. While the spatial resolution of the generated x-rays is much worse than electrons due to the larger escape region, they can be used to determine the elements present and therefore generate elemental maps, where the presence of each element is given false color on the final image to show its distribution across the image. This process is known as energy-dispersive x-ray spectroscopy (EDS). Figure 2.9 illustrates the focusing of the primary beam and collection of secondary electrons.

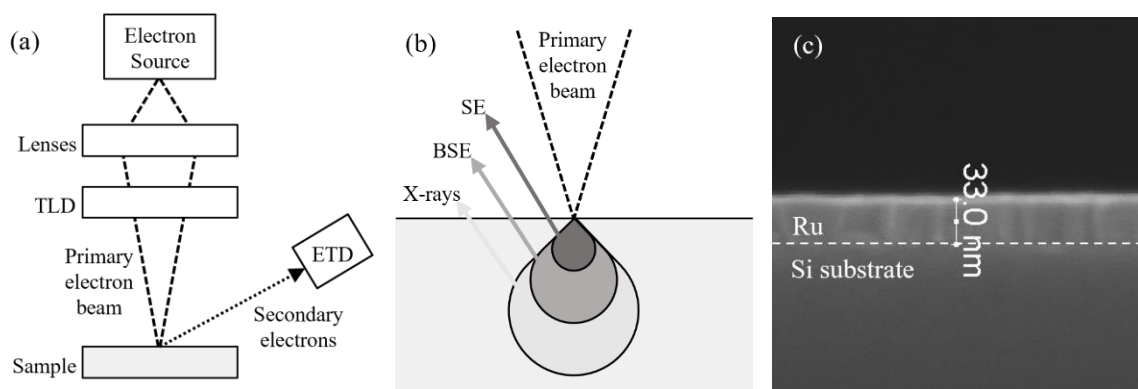


Figure 2.9. (a) Schematic of SEM image collection. The lenses focus the primary beam and raster scan it across the sample, and secondary electrons are collected in the TLD or ETD detectors. (b) Illustration of the depth of electrons and light generated by the primary electron beam. As the escape depth of the phenomena increase, the resolution of the image lowers as a greater area is affected. (c) SEM image of an as-rec. Ru sample. The Ru and Si substrate, as well as thickness are labelled manually.

With SEM imaging, the thickness of the film can directly be measured, rather than needing to be derived. However, the accuracy of thickness measurements is limited by the resolution, as well as any artifacts of the process, such as charging and material contrast. In addition, samples must be cleaved close to the imaging time, as particles and contaminants from the ambient can stick to the surface and obscure or distort the image.

To determine the thickness of films, SEM images were taken using a FEI Nova 600 with 10 kV accelerating voltage and 0.54 nA beam current using the through-lens detector. The thickness of a sample was determined by taking the mean of several measurements taken across the cross-section of the sample, with the error bars representing the standard deviation of the measurements. To find the etch rates, a linear regression weighted by the uncertainty of each data point was performed. The slope of the regression line was taken to be the etch rate with uncertainty equal to the standard error of the slope. To determine if an etch rate determined by this method

significantly differed from zero, the t -value was determined by the formula $t = \beta / s\sqrt{n}$ where β is the slope, s is the standard deviation and n is the number of data points, with degrees of freedom equal to $n - 2$ used to determine the p -value. To determine if two etch rates taken from separate datasets were significantly different from each other, the z -value was $z = (\beta_1 - \beta_2) / \sqrt{s_1^2/n_1 + s_2^2/n_2}$ (Clogg et al., 1995). In both cases, the threshold for significance, α , was taken to be <0.05 .

2.4.2 Profile of Patterned Samples

While SEM is a powerful technique for nanoscale imaging, its resolution is limited by the size of the escape region where secondary or backscattered electrons can arise from. To reach atomic-scale resolution, a similar technique, transmission electron microscopy (TEM) is used. In this setup, transmitted electrons are detected after passing through a thin (10-100s of nm) sample, improving the resolution. There are two primary methods for generating an image from transmitted electrons, conventional TEM and scanning TEM (STEM). In TEM, the incident electron beam is collimated into a parallel beam that strikes the surface and the transmitted electrons are simultaneously collected to form an image. In STEM, a raster image is formed by instead focusing and scanning the electron beam across the sample, akin to the raster used in SEM. The contrast of the image can be caused by different electron interactions depending on the collection method. Bright field TEM captures transmitted electrons, so bright regions correspond to high amounts of transmitted electrons. The transmission amplitude is reduced by increasing thickness and/or mass, so the contrast is termed mass-thickness. Because the electron beam is coherent and monochromatic, diffraction on crystal planes present in the target can occur. The resulting electron

diffraction pattern can be imaged, allowing the crystal structure to be determined. Alternatively, a diffracted beam can be collected, resulting in dark field images, as regions where no diffraction occurs are dark. At positions where the Bragg condition is fulfilled, the electrons diffract and are detected, resulting in contrast according to the satisfaction of the condition. High resolution TEM (HRTEM) instead utilizes phase contrast, where differing phases lead to destructive or constructive interference leads to a change in amplitude that can be detected to form an image with angstrom-level resolution that can discern individual atoms.

In STEM configurations, additional collection methods are possible. One method is high angle annular dark field imaging (HAADF-STEM), where an annular detector is used. Since this detector does not have spatial resolution, scanning is required to produce the image. The scattering of high angle electrons is proportional to the atomic number of the target elements, so HAADF provides Z-contrast, like backscatter SEM. Using an x-ray detector, EDS images can be collected using STEM configuration, rather than SEM. Because the sample must be prepared for TEM by thinning, the x-rays generated by the incident beam originate from a smaller region within the sample, improving the resolution.

Using patterned samples with pitches below 20 nm, SEM imaging no longer provides the resolution needed to measure the thickness and width of patterned features, as well as additional parameters such as sidewall angle that are derived from the profile. In this work, HRTEM was used to image sets of these patterned samples in order to systematically measure feature profiles.

To extract the profile from a TEM image, it is necessary to differentiate the Ru features from the substrate, hard mask, and protective carbon layer. Image processing was done using Python and its OpenCV library, allowing batch processing of TEM images to be done. Due to mass

contrast, Ru appears darker compared to the other materials present in the TEM, providing the potential for a thresholding operation to isolate the areas where Ru is present. Before this can be done a denoising operation must be applied, as there is variation in the values of the other regions - particularly the carbon layer - that result in pixels dark enough to meet the threshold. A common method for denoising is done by blurring the image, where each pixel's value is averaged to the pixels surrounding it. A Gaussian blur uses Gaussian curves centered on the pixel as weight for the average, which removes noise at the cost of sharpness, as small features are averaged out. At the edges of the Ru features in the TEM images, this causes a loss of information as they smoothed by the blur. To improve the contrast of edges, a bilateral blur can be used instead. The bilateral blur iterates on the Gaussian blur by weighting based on the intensity difference of the center pixel compared to the surrounding pixels. This reduces the effect that pixels with highly different values have on the average, resulting in preservation of edges where the contrast is high. After these denoising steps, the image is thresholded to separate out the areas where Ru is present. The resulting shapes represent the Ru features, but can be measured to determine the film thickness, feature width, and other measurements systematically. This allows etch rates to be measured in the vertical as well as the horizontal direction, and the profile of the hard mask to be plotted.

To extract the dimensions of the hard mask, it is necessary to perform additional processing, as SiO_2 appears with similar contrast to the protective layer. However, the frequency of the variations in the lightness of the two materials can be used to determine the edges of the hard mask. By performing a Gaussian blur with large enough radius to smooth out the variations in the hard mask, but too small to fully smooth out the variations in the protective layer, a threshold can be applied to the image. The hard mask is fully black in the threshold, but the surrounding area

has patches of black and white. Because the black regions are small, a shrink and expand operation can be used to remove all of the black regions that are smaller than the magnitude of each operation. This removes the black patches but retains the black region of the hard mask. However, this operation causes a loss of resolution as small features are smoothed. Because of this, the exact profile of the hard mask cannot be extracted. Instead, the horizontal width and vertical height of the hard mask can be estimated by averaging each row or column of the image to maximize the signal to noise ratio. Because this causes the loss of a dimension, only the width and height of the hard mask can be extracted from the image. In profiles of features extracted from TEM in this work, the hard mask is represented schematically as a rectangle with the dimensions extracted by the above process.

Since the image processing technique can efficiently be applied to multiple features, uncertainty in results determined by TEM were taken to be the standard deviation of the measurement across all identical features.

2.4.3 Surface Composition and Chemical State

X-ray photoelectron spectroscopy (XPS) is a powerful technique that can be used to determine the surface chemistry of a sample, including both the elemental composition and the bonding state. By exposing a surface to high energy light, photoelectrons are released. The kinetic energy of a photoelectron can be determined from the energy of light and the binding energy of its orbital,

$$E_{kin} = h\nu - E_{bind} - \phi \quad (2.11)$$

where ϕ is the work function of the spectrometer. By generating x-rays at a specific energy and measuring the kinetic energy of resulting photoelectrons, the binding energy of electrons in the

sample can be determined. Monochromatic x-rays can be generated by striking a single element target with high energy electrons, which causes the ejection of electrons from the core level. An electron from higher energy levels fills the core level vacancy while emitting light at an energy equal to the difference in energy levels. This light is passed through a filter to remove light emissions at other wavelengths. In this work, x-rays at 1486.6 eV generated from the $k\text{-}\alpha_1$ transition of Al are used in XPS.

The XPS spectrum of an element is determined by its characteristic energy levels, and multiple peaks corresponding to different orbitals appear. Additional electrons can be ejected through the Auger process, as energy generated by the filling of a core level hole can cause an outer electron to eject. These Auger electrons have a kinetic energy that is independent of the x-ray energy, unlike photoelectrons, but are still characteristic to the element they originate from. Additional effects can modify the binding energy that peaks appear at. Spin orbital splitting is caused by the slight difference in energy between electron in the same orbital, but with differing total angular momentum numbers, j , which is the absolute sum of the orbital angular momentum, l , and the spin angular momentum, s . For s-shell electrons, which have $l = 0$, $j = |0 \pm \frac{1}{2}| = \frac{1}{2}$, so there is no spin orbital splitting. For other shells, two values of j with different energy are possible, $l + \frac{1}{2}$ and $l - \frac{1}{2}$. The states have a degeneracy of $2j + 1$, so the ratio of the number of electrons in each state can be expressed as $\frac{2l+2}{2l}$. This ratio corresponds to the ratio of peak area in spin-orbital splitting seen in XPS. The kinetic energy of a photoelectron is affected by the charge density around the atom, so the chemical state of the atom – oxidation state and electronegativity of atoms bonded to it – causes a shift in the binding energy.

In XPS equipment, electrons are detected by a hemispherical analyzer that slows electrons with specific kinetic energy down to the pass energy. These electrons only reach the detector when they match the pass energy, so by sweeping across the range of possible kinetic energy values, a spectrum can be recorded. The pass energy is an instrumental parameter that is proportional to the signal-to-noise ratio and inversely proportional to the energy resolution. High pass energy is used to collect spectra over a wide binding energy range where low resolution is a valid tradeoff for increased signal. Low pass energy is used for detailed scans of a single peak, where high resolution is needed to differentiate individual peaks with similar binding energies.

Once an XPS spectrum is collected, qualitative determination of the composition can be done by comparing the binding energy of peaks to literature values for each element. Each peak for each element has a relative sensitivity factor (RSF), which is a dimensionless number that compares the likelihood of photoelectron generation and therefore peak area. While a peak is present for each orbital around an atom of an element, generally a single peak is used for quantification and detailed analysis per element, usually the most intense one. For common elements such as C, N, O and F, this is the 1s peak, while for higher atomic number elements through the first transition metal row, the 2p peak is preferred. The area under each peak represents its intensity and can be normalized by dividing by its RSF to get the relative intensity. The atomic composition can be found by dividing each relative intensity by the sum of all relative intensity. Beyond this, a peak can be deconvoluted into multiple peaks, often using a symmetrical Gaussian-Lorentzian peak to represent electrons atoms in multiple chemical states and spin orbital splitting. This allows the chemical state of the element to be determined, even if it is present in multiple overlapping states on the surface. Figure 2.10 is XPS spectra of the Ru 3d, N 1s, and O 1s regions

of Ru, RuN, and RuO₂ thin films. Within a region, the peak shape varies as the proportion of metal Ru and its oxides and nitrides varies. The presence of RuN is confirmed by the corresponding peak in the N 1s region.

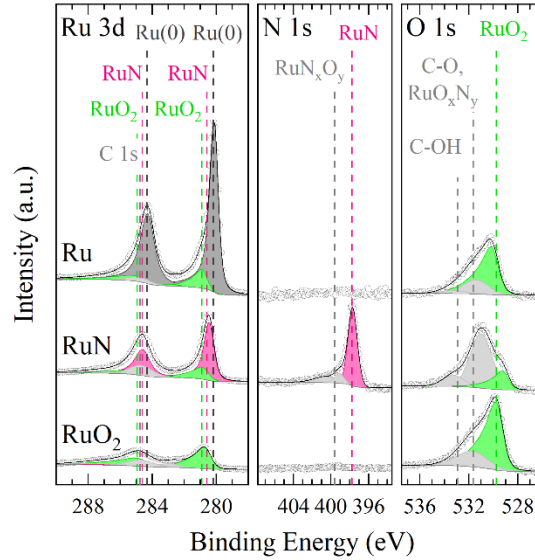


Figure 2.10. X-ray photoelectron spectra of Ru 3d, N 1s, and O 1s regions of as-deposited Ru, RuN, and RuO₂. Peaks corresponding to Ru-N bonding and Ru-O bonding are highlighted. XPS was performed *ex-situ*, resulting in the formation of native oxide on the Ru and RuN samples prior to characterization.

The amount of RuO₂ and/or RuN present as a thin layer on top of Ru films after plasma processing was measured in thickness. These layers were not distinguishable from Ru in the SEM images, so the thickness was determined using the areas of the Ru, RuO₂, and RuN XPS peaks in the Ru 3d region. The intensity of a peak is given as $I = K \int_0^\infty C(x) \exp\left(-\frac{x}{L}\right) dx$ where K is an instrument-specific constant, C is the atomic density of the element as a function of depth, x , and L is the effective attenuation length (EAL), which is used in place of the inelastic mean free path (IMFP) to account for elastic scattering. The EALs and atomic density used are given in Table 2.6. This equation can be used to determine the thickness of thin films, provided that the thickness is

less than the detection limit of the XPS. Given a native Ru oxide layer with thickness t , the integrals can be solved for the oxide and underlying Ru layers to give

$$I_{RuO_2} = KC_{RuO_2}L_{RuO_2} (1 - \exp(-t/L_{RuO_2})) \quad (2.12)$$

$$I_{Ru} = KC_{Ru}L_{Ru} \exp(-t/L_{Ru}) \quad (2.13)$$

which can be combined to find the oxide layer thickness

$$t = L_{RuO_2} \ln \left(\frac{I_{RuO_2}C_{Ru}L_{Ru}}{I_{Ru}C_{RuO_2}L_{RuO_2}} + 1 \right) \quad (2.14)$$

assuming the EALs are approximately equal, as in the case of Ru and RuO₂. The thickness of the native oxide layer on an as-received Ru film was found to be 0.7 nm with this method.

Table 2.6. Parameters used to determine the thickness of Ru, RuO₂, and RuN films. The effective attenuation lengths were determined from the NIST SRD 82(Jablonski & Powell, 2009) for electrons with a kinetic energy of 1206 eV, corresponding to the Ru 3d5/2 peak in XPS using Al K α x-rays.

Material	Ru atomic density (#/nm ³)	EAL (nm)
Ru	73.8	2.34
RuO ₂	30.5	2.49
RuN	42.1	2.42

Equation 2.14 can be extended to three layers, such as in the case where the substrate layer is Ru and plasma nitridation forms a surface layer of RuN, which is subsequently oxidized in ambient. In this case, there is a layer of Ru oxide, Ru nitride, and the underlying Ru. The thickness of layers t_{RuO_2} and t_{RuN} are found to be

$$t_{RuO_2} = L_{RuO_2} \ln \left(\frac{I_{RuO_2}/C_{RuO_2}L_{RuO_2}}{\frac{I_{Ru}}{C_{Ru}L_{Ru}} + \frac{I_{RuN}}{C_{RuN}L_{RuN}}} + 1 \right) \quad (2.15)$$

$$t_{RuN} = L_{RuN} \ln \left(\frac{\frac{I_{RuO_2}}{C_{RuO_2}L_{RuO_2}} + \frac{I_{RuN}}{C_{RuN}L_{RuN}}}{\frac{I_{Ru}}{C_{Ru}L_{Ru}}} + 1 \right) - t_{RuO_2} \quad (2.16)$$

In addition to determining the amount of RuN formed by plasma nitridation, the same process can be used to determine the amount of RuN reduced into Ru by H₂ plasma, by switching the Ru and RuN layers in the model. Two example results are shown in Figure 2.11.

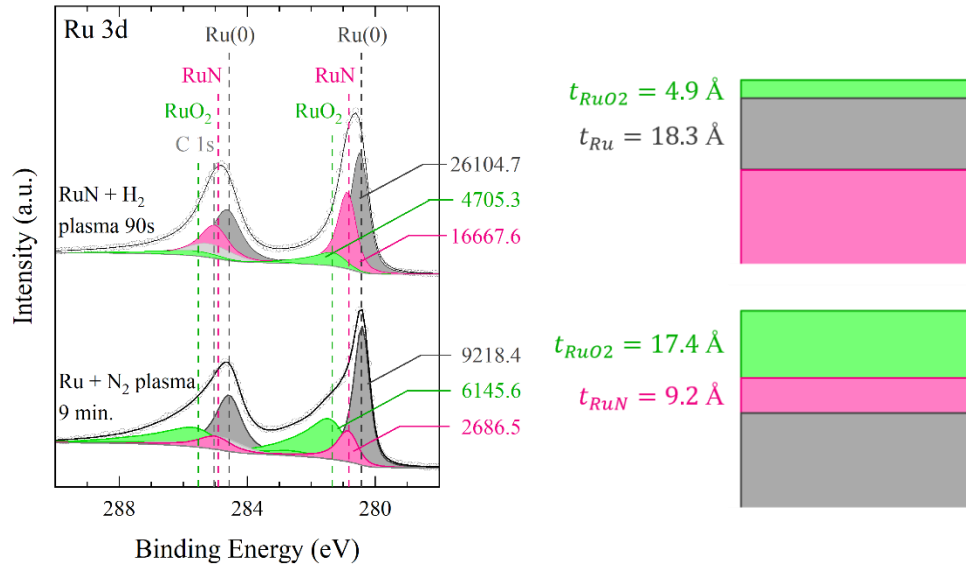


Figure 2.11. XPS detailed scan of Ru 3d region for a RuN sample with a reduced Ru layer, and Ru sample with a nitridated RuN layer. In both samples, there is a layer of native oxide present on the film. Using the area of the peaks corresponding to Ru, RuO₂, and RuN, the thickness of each layer can be found.

In this work, XPS scans were collected with a Kratos Axis Ultra system. The x-rays were generated using a 10 mA emission current on an Al K- α_1 (1486.6 eV) target, and the photoelectrons were collected at a pass energy of 160 eV for survey scans, and 40 eV for detailed scans. A

neutralizer was used to measure insulating samples to correct for sample charging, and an Ar ion beam was used to etch samples for depth profiling. Uncertainty in the area and resulting thickness values were found using the CasaXPS Monte Carlo error analysis. A covariance matrix was generated for each parameter of the peak-fitting model (peak area, binding energy, and FWHM), and the variance in peak area was used to propagate error to the film thickness equations.

2.4.4 Crystal Structure

Structural characterization of a crystalline solid can be done with x-ray diffraction (XRD). Like XPS, monochromatic x-rays strike the sample surface, but rather than measuring the resultant photoelectrons, XRD relies on measuring the x-rays after diffracting on the surface. As the angle of the incident x-ray beam is varied, interference between beams reflecting off crystal planes within the film causes the intensity of the reflected beam to vary. At the Bragg angle, constructive interference causes the intensity to peak. The Bragg angle, θ , is dependent on the interlayer spacing of the crystal, d , and wavelength of the x-ray, λ ,

$$n\lambda/d = 2\sin\theta \quad (2.17)$$

where $n = 1, 2, 3 \dots$. The interlayer spacing is determined by the particular crystal plane of the reflection and the structural parameters of the crystal. XRD commonly uses Cu $k\text{-}\alpha_1$ x-rays with a wavelength of 1.5406 Å, including in this work.

In the theta-2theta alignment, the angle between the source and detector, 2θ , and the source and sample surface, ω , is swept while keeping $\theta = \omega$. In this configuration, peaks in the detected intensity correspond to reflections from crystal planes parallel to the surface. In a poly crystalline

substance, such as a powder, this includes all of the planes present in the crystal, while in thin film samples with a single-crystal or highly aligned crystals, only certain planes may reflect due to the alignment of the crystal grains. The interlayer spacing can be used to calculate the lattice parameters of the crystal given that the plane indices are known.

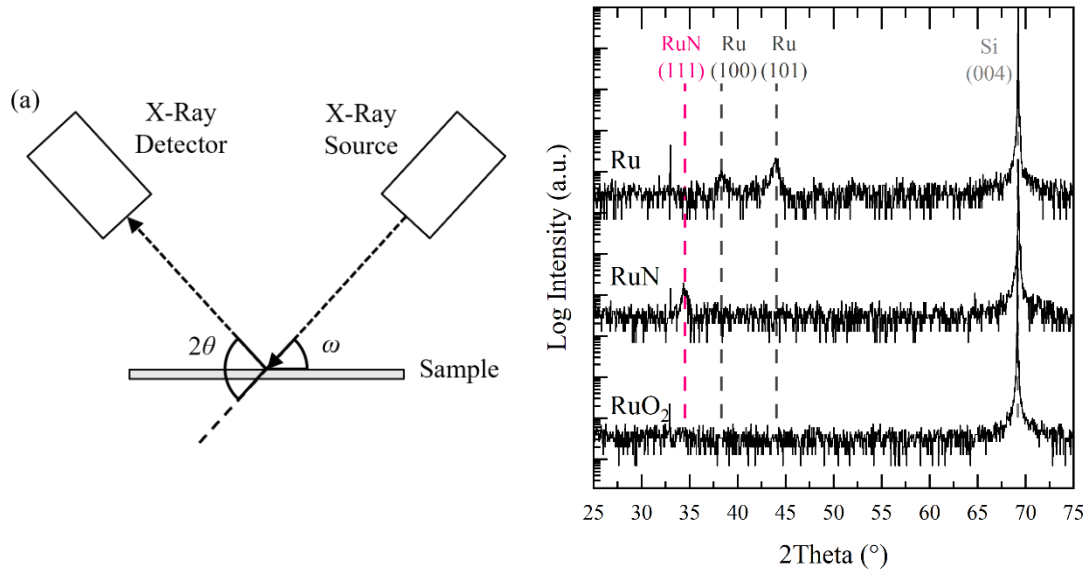


Figure 2.12. (a) Schematic of XRD system in theta-2theta configuration, where $\theta = \omega$. (b) XRD scans of as-deposited Ru, RuN, and RuO₂. Peaks corresponding to Ru and RuN are present in their respective scans, and the (004) Si peak appears from the substrate.

XRD measurements were collected with a Bede D1 diffractometer using a Cu $k\alpha_1$ x-ray source (1.54066 Å) with a double crystal monochromator. The monochromator removes unwanted wavelengths by passing the beam through two Si crystals at the Bragg angle for the primary wavelength. XRD scans were taken in the theta-2theta alignment. XRD scans of as-deposited Ru, RuN, and RuO₂ films are shown in Figure 2.12.

2.4.5 Surface Roughness

Atomic Force Microscopy (AFM) enables the characterization of surface topography and quantification of the surface roughness. In AFM, a nanoscale tip machined from Si is raster scanned across a region of the sample. This tip is deflected by the surface topography of the sample, with the height of the sample measured by the displacement of a laser reflected off the back of the AFM tip. During the scan, the tip can be in contact mode, where it remains on the surface, or in tapping mode, where it makes contact only briefly with the surface as it scans. In tapping mode, the amplitude of the movement of the tip is used to determine the height. The raster scan provides a two dimensional mapping of the height of the surface, which can be analyzed using statistical methods to obtain a measure of roughness. Surface roughness of thin films is primarily reported as the root-mean-square,

$$R_q = \sqrt{\frac{1}{A} \iint Z^2(x, y) dx dy} \quad (2.18)$$

where A is the area being measured and Z is the height at point (x, y) .

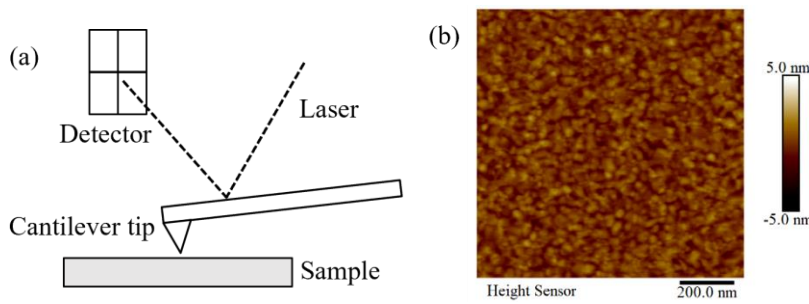


Figure 2.13. (a) Schematic of AFM, where the displacement of a laser reflected off the cantilever tip is used to determine the surface height as the tip raster scans the surface. (b) Image of AFM heightmap of an as-rec. Ru sample with RMS roughness of 0.64 nm.

A Bruker Dimension FastScan was used to collect AFM data, which was analyzed using the Nanoscope Analysis software. Scans were taken on a 1 μm square area with a scan rate of 3.76 Hz and a drive amplitude of 50 mV.

2.4.6 Resistivity

The resistivity of a blanket film sample is measured by four-point probe (4PP). The 4PP is used to measure the sheet resistance using four equally spaced probes. In this configuration, a current, I , is applied through the two outer probes, while the inner two probes are used to measure the voltage difference, ΔV . This eliminates the contribution of contact resistance between the probes and thin film from the resulting value, giving the sheet resistance

$$R_s = C \frac{\pi}{\ln 2} \frac{\Delta V}{I} \quad (2.19)$$

where C is the correction factor, which accounts for the geometry of the sample. When the dimensions of the sample are similar in magnitude to the spacing between the probes, the correction factor is necessary to record an accurate value. Sheet resistance is related to bulk resistance, R (generally known simply as resistance), and resistivity, ρ , by the equations

$$R_s = R \frac{W}{L} = \frac{\rho}{t} \quad (2.20)$$

where W is the width and L is the length of the area measured. While sheet resistance has units of Ohms, to differentiate it from bulk resistance, the units are referred to as Ohms per square, as a square ($W = L$) object has equal sheet and bulk resistance. The sheet resistance is proportional to the thickness of the film, while resistivity is generally independent of the thickness, except at the

sub 100 nm range where surface and grain boundaries scattering effects become relevant. Since the four-point probe measures sheet resistance, it is necessary to know the thickness of the film to obtain the resistivity.

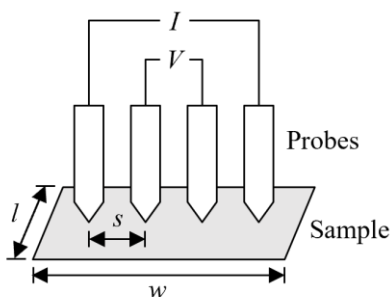


Figure 2.14. Schematic of a four point probe. The current is passed through the outer probes, allowing the inner probes to measure the voltage to determine the resistance. The dimensions of the probes and sample are necessary to determine the geometric correction factor.

2.5 Summary

The samples prepared, processed, and characterized as described above have been used to determine the results demonstrated in chapters 3, 4, and 5. In chapter 3, the blanket film Ru samples were exposed to plasma using OES diagnostics and characterization of the etched samples' thickness, surface composition, roughness, and resistivity in order to determine the effects of each plasma chemistry separately and as a cyclic process.

Chapter 3. Plasma Processing for Surface Modification of Ruthenium

To develop a process capable of etching Ru with high anisotropy and low selectivity, it is first necessary to understand the effects of individual plasma processes on Ru surfaces. While O₂ plasma etching of Ru has been studied for many years, the potential for passivation by plasma nitridation has not been explored previously. After establishing the effect of the baseline O₂ plasma process on Ru, plasma nitridation of Ru in N₂ plasma was demonstrated with the formation of thin layers of RuN on Ru. This nitridated layer was confirmed using XPS, with its thickness reaching as high as 1 nm. This thin layer of RuN was sufficient to protect the film from O₂ plasma, delaying the onset of etching by 3 minutes. To remove the RuN layer, H₂ plasma was shown to effectively remove both RuO₂ and RuN from the surface. The combined cyclic etch process consisted of sequential exposure to N₂ plasma, H₂ plasma, and O₂ plasma. On blanket films, this resulted in an etch rate of 3.6 nm per cycle. When ions were blocked from reaching the surface, RuN formed during the nitridation step was not fully removed by the H₂ reduction step, which allowed it to passivate the surface from etching by O radicals. Compared to continuous O₂ plasma, the ratio of etch rates with or without ions was increased from 4.6 to 18, providing a pathway for anisotropic etching of Ru through surface modification.

3.1 Etching Ru with O₂ Plasma

The baseline condition used in this work was continuous O₂ plasma generated in an ICP chamber with 500W ICP power, 30 mTorr, and no bias. Due to the formation of Ru tetroxide, which has a boiling point at 40°C and favorable free energy of reaction with O radicals, Ru is easily etched in O₂ plasma. To confirm this, an O₂ plasma was monitored by optical emission spectroscopy with or without a Ru sample present in the chamber, as shown in Figure 3.1(a). In

both cases, prominent peaks corresponding to the atomic O transition $3p \rightarrow 3s$ appear at 777 and 844 nm. In addition, molecular N_2 peaks appear from the purge cycle prior to O_2 exposure. When Ru is present in the chamber, additional peaks appear in the 300-475 nm region that correspond to atomic Ru. The difference spectra between the O_2 plasma with and without Ru is shown as the red area in Figure 3.1(b) and fits well with the literature reported peak intensity for atomic Ru, confirming that etching is occurring.

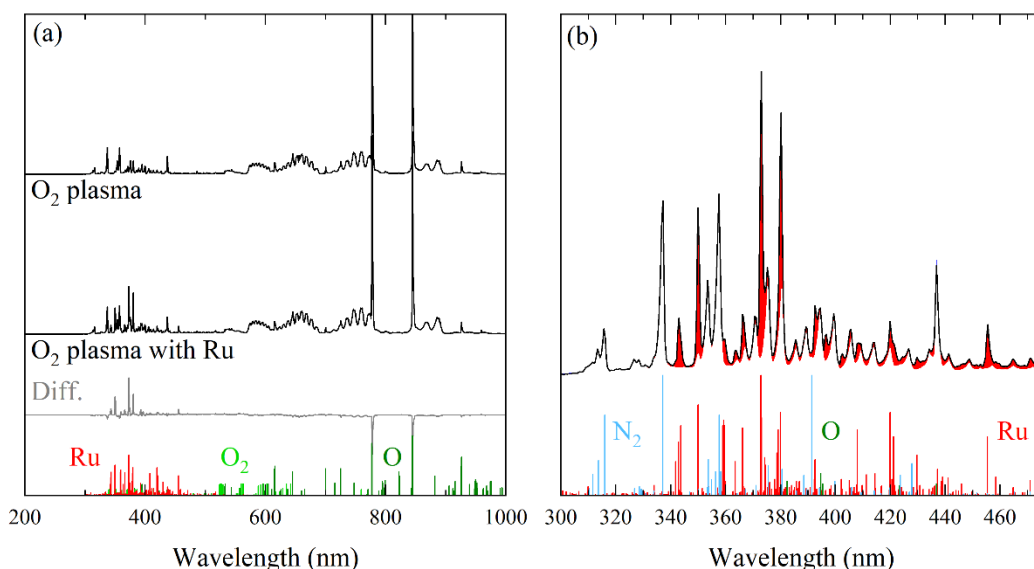


Figure 3.1. (a) Optical emission spectroscopy of O_2 plasma. The difference spectrum between the spectra with and without Ru present in the chamber is shown in gray. Peaks corresponding to atomic Ru can be seen in the difference spectrum, indicating that Ru is being etched. (b) Inset of the 300 – 475 nm region where peaks can be seen. The difference between the two spectra is highlighted in red and matches with the literature values for atomic Ru.

The major effect of O_2 plasma on Ru surfaces was oxidation to RuO_2 and etching. To understand the effect of plasma conditions, and the underlying plasma parameters, on the etch rate, the power and pressure were varied from 300 – 800W, and 15 – 50 mTorr, respectively, in Figure 3.2. The strong dependence of the etch rate on power indicates that the plasma density affects the

etch rate most significantly, and the Chemkin model of O₂ plasma confirms that n_e , the electron density, which is equivalent to the ion density due to the quasi-neutrality of plasma, is most significantly affected by power. On the other hand, while electron temperature increases as pressure decreases, increasing the dissociation fraction of O₂, it has little effect on the etch rate.

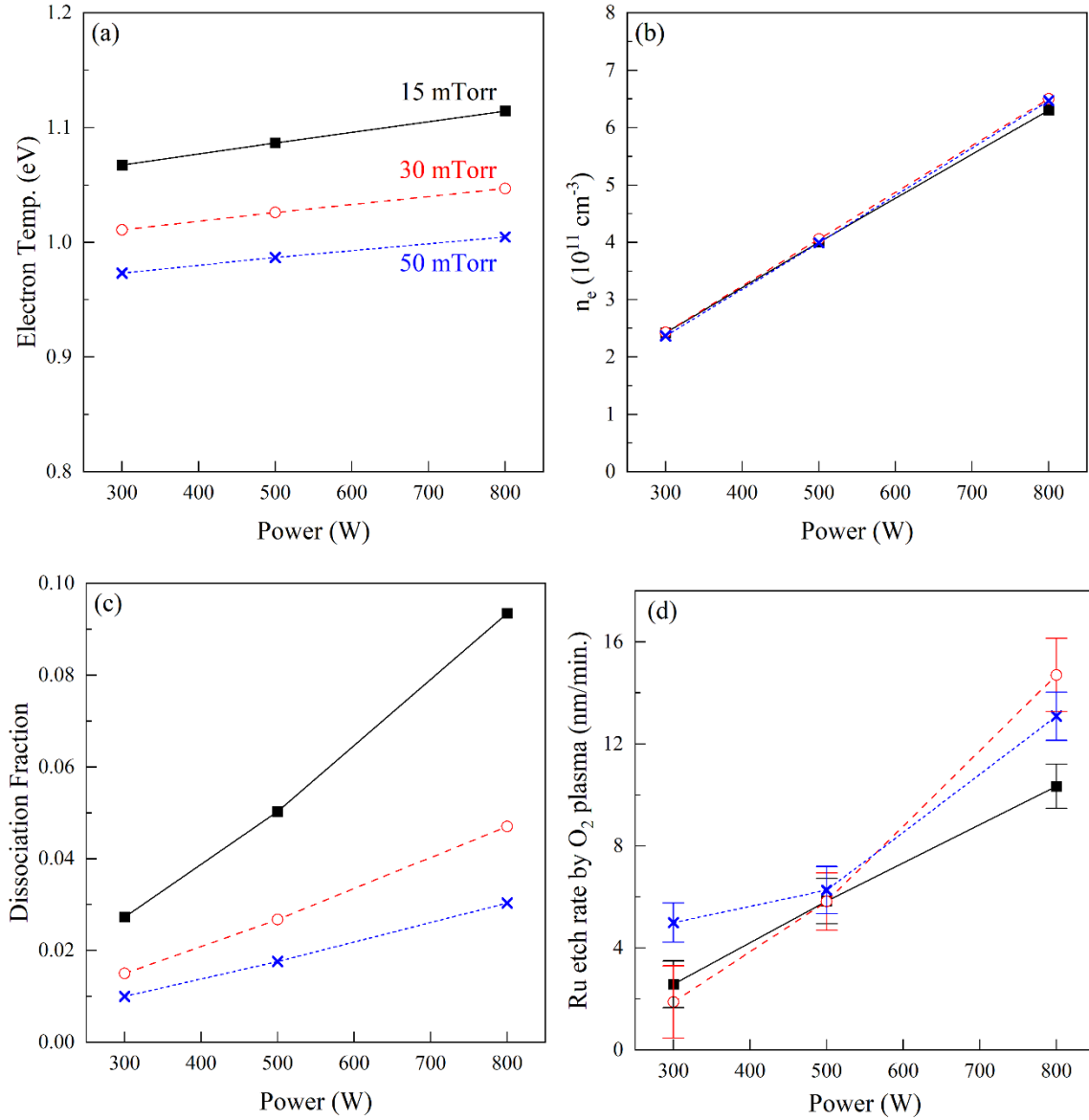


Figure 3.2. Plasma parameters from Chemkin simulation of O_2 plasma. (a) Electron temperature is mainly dependent on pressure, while (b) electron (and ion) density is dependent on power. (c) Dissociation fraction of O_2 is dependent on both power and pressure. (d) Experimentally determined etch rate of Ru in O_2 plasma, which correlates with primarily with the ion density.

Because of the lack of applied bias, the energy of ions in the O_2 plasma was below the threshold sputtering energy of 26 eV for O_2^+ , and 28 eV for O^+ . This means that the increase to etch rate with increased ion density is not due to an increase in sputtering of the Ru itself. Instead,

the O radicals were able to oxidize Ru, forming higher stoichiometry Ru oxides that are then removed from the surface by ions, with the limiting step coming from the ion-enhanced desorption of RuO₃ or RuO₄ from the surface, rather than the oxidation itself.

This is further confirmed by comparison of samples etched by O₂ plasma with or without ions using a Si shield that physically blocks ions, while allowing radicals to reach the surface. Compared to the as-deposited Ru surface, more RuO₂ is formed as the oxidation time increases, though the rate of formation is reduced as the thicker oxide layer causes slower diffusion of the Ru or O atoms to the surface or metal-oxide interface, respectively. In addition, the continual etch of the surface serves to have the oxide layer reach a steady state where the etch rate is equal to the rate of new oxide formation. As evidenced by Figure 3.3, an equivalent or thicker amount of oxide is formed on the surface when ions do not reach the surface, confirming that radicals are effective at oxidizing the surface even when ions do not reach the surface.

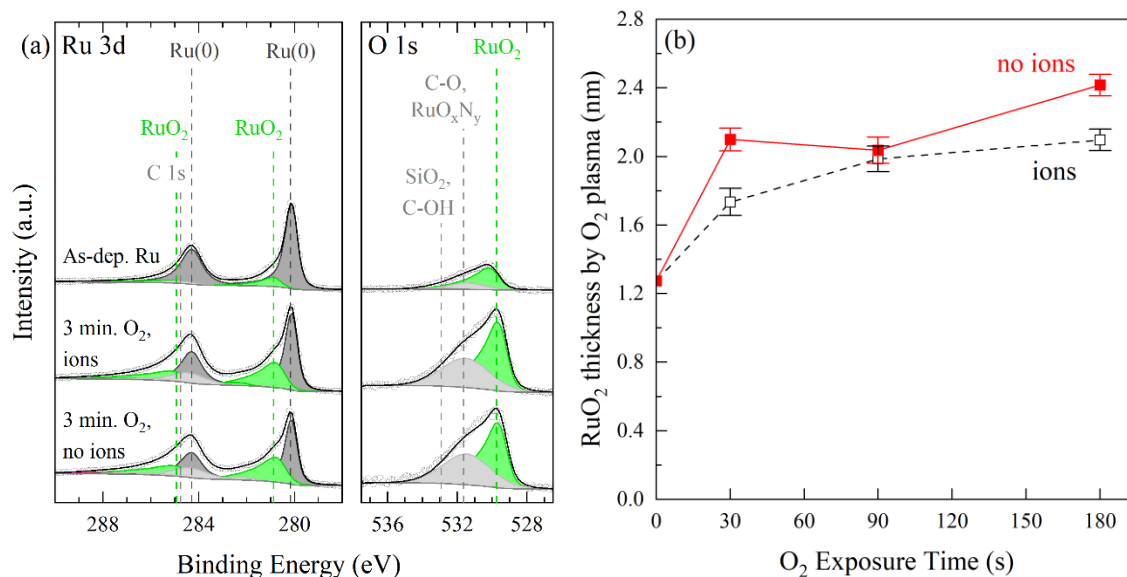


Figure 3.3. (a) X-ray photoelectron spectra of Ru samples exposed to O₂ plasma with and without ions. (b) The thickness of the surface RuO₂ layer is similar whether or not ions are present, indicating that the oxidation of the Ru surface is done by O radicals.

Without ions, the etch rate is lower, as seen in Figure 3.4. This corresponds to the reduced ability of RuO₄ without ion enhancement. Alternatively, increasing the applied bias power increases the energy of electrons reaching the surface, allowing the Ru itself to be sputtered in tandem with chemical etching of Ru. The ratio of ion-enabled vs. radical only etching is 4.6, representing the increased removal of RuO₄ from the surface as low energy ions strike the surface.

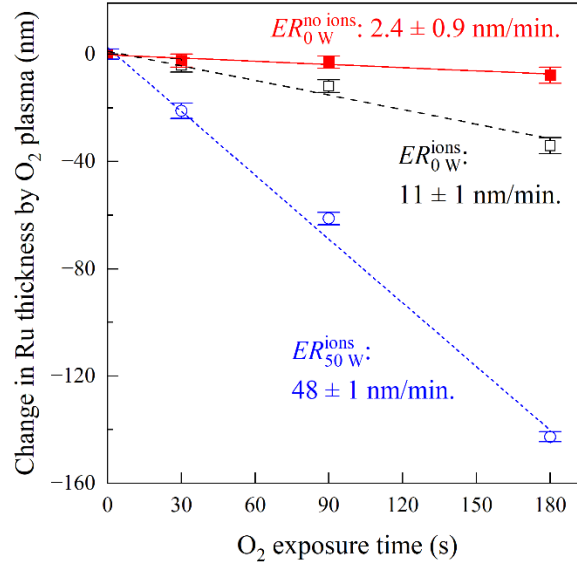


Figure 3.4. Etch rate of Ru in O₂ plasma with the bias power and presence of ions varied. Without ions, O radicals are able to etch the Ru, but with ions the etch rate is increased, particularly when the ion energy is increased by increasing the bias power.

3.2 Passivation of Ru with Plasma Nitridation

For the proposed three-step process, N₂ plasma must be able to form the metastable RuN, and the RuN layer must passivate against etching by O₂ plasma. While the oxidation of RuN into RuO₂ is favorable when reacting with O radicals, the Ru-N bond is predicted to be 4.9 eV, while the Ru-Ru bond is only 2.0 eV. This difference suggests that the activation energy for the oxidation of RuN may be higher than for Ru, lowering the oxidation reaction rate, and therefore, the overall etch rate.

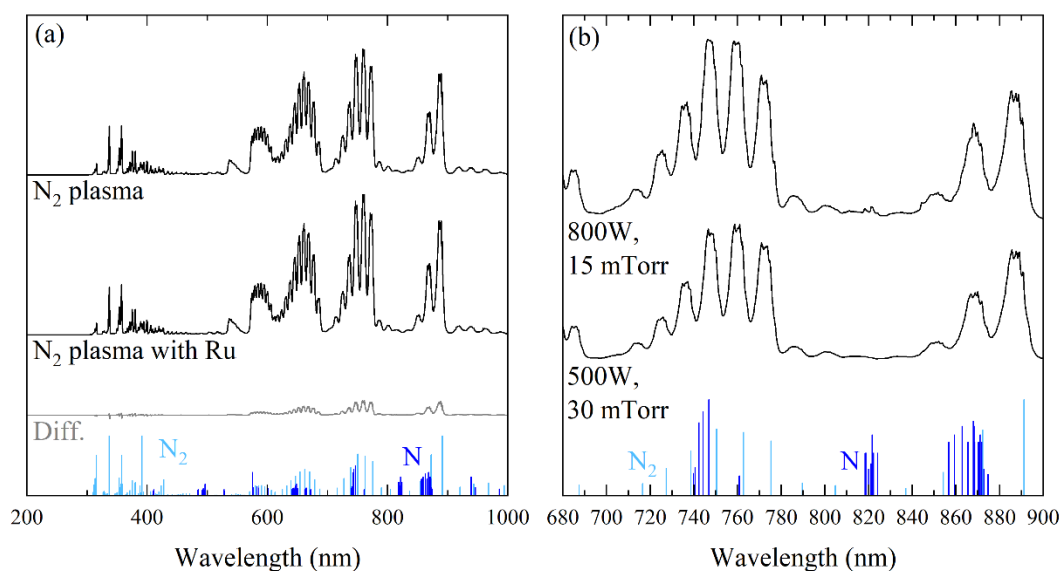


Figure 3.5. (a) Optical emission spectroscopy of N₂ plasma. The difference spectrum between the spectra with and without Ru present in the chamber is shown in gray. The lack of peaks corresponding to Ru indicate that Ru is not being etched during N₂ plasma exposure, with only slight differences in the intensity of N₂ peaks appearing. (b) Optical emission spectra of N₂ plasma in the 700 – 900 nm. Peaks corresponding to atomic N can be seen at higher power and lower pressure, where the dissociation fraction is the highest.

To establish the effects of N₂ plasma on Ru, the optical emission spectra of the plasma with or without Ru present was found in Figure 3.5. No atomic Ru was found in the spectra, and instead, the main species seen was molecular nitrogen in the form of the first ($B^3\Pi_g \rightarrow A^3\Sigma_u^+$, 500 – 900 nm) and second ($C^3\Pi_u \rightarrow B^3\Pi_g$, 300 – 350 nm) positive systems, two broad bands of peaks corresponding to varying vibrational excitation states underdoing an electronic transition. Atomic N peaks at 821, 868, and 939 nm are very faint, and can only be distinguished when the plasma is run at 800W or 15 mTorr. While the exact composition of the plasma cannot be determined from OES without actinometry, the relative intensity of the molecular N₂ bands indicates that the plasma is largely undissociated.

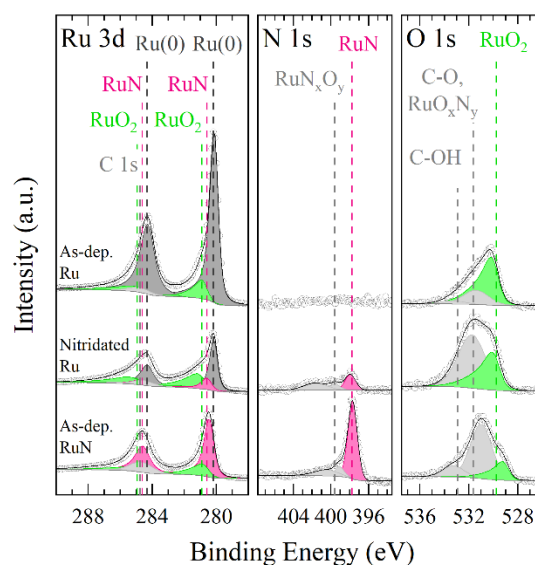


Figure 3.6. X-ray photoelectron spectra of plasma nitridated Ru compared to the as-deposited Ru and RuN. The presence of Ru⁰ and RuN peaks confirms the formation of a thin layer of RuN on the Ru film.

X-ray photoelectron spectroscopy was used to measure the amount of plasma nitridation of Ru by assuming a layer structure of RuO₂/RuN/Ru. Since samples were exposed to air between nitridation and XPS, native oxide formed on the surface, necessitating the use of a third layer for fitting XPS areal intensity. The assumption was made that Ru-N bonding on the surface resulted in the formation of a stoichiometric layer, as evidenced by the presence of peaks in the Ru 3d and N 1s region at the same binding energy as the bulk, stoichiometric RuN deposited, as can be seen in Figure 3.6. From the XPS intensity model, 1 nm of RuN was found to form as a result of plasma nitridation.

As was done for plasma oxidation and etching, the amount of RuN formed on the surface was measured as a function of plasma power and pressure. Unlike the case of O₂ plasma, the biggest contribution to increasing RuN thickness was through decreasing the pressure. From the Chemkin model shown in Figure 3.7, the electron temperature, and relatedly, N₂ dissociation

fraction, are closely related to the amount of RuN formed experimentally. This suggests that the ion density has little impact on the formation of the RuN layer, but increasing electron temperature is more important due to the high threshold energy of N₂ dissociation, 9.8 eV, resulting in a lower concentration of N atoms compared to the O atoms in the O₂ plasma. In addition, the higher electron temperature encourages increased numbers of excited N₂ species, which can dissociate on the Ru surface with a higher sticking coefficient due to the lower energy barrier between the electronically and/or vibrationally excited state, and the dissociated state (Rouwenhorst & Lefferts, 2021). This finding correlates well with the optical spectroscopy of the N₂ plasma, which finds only small concentrations of atomic N peaks, while molecular N₂ bands dominate.

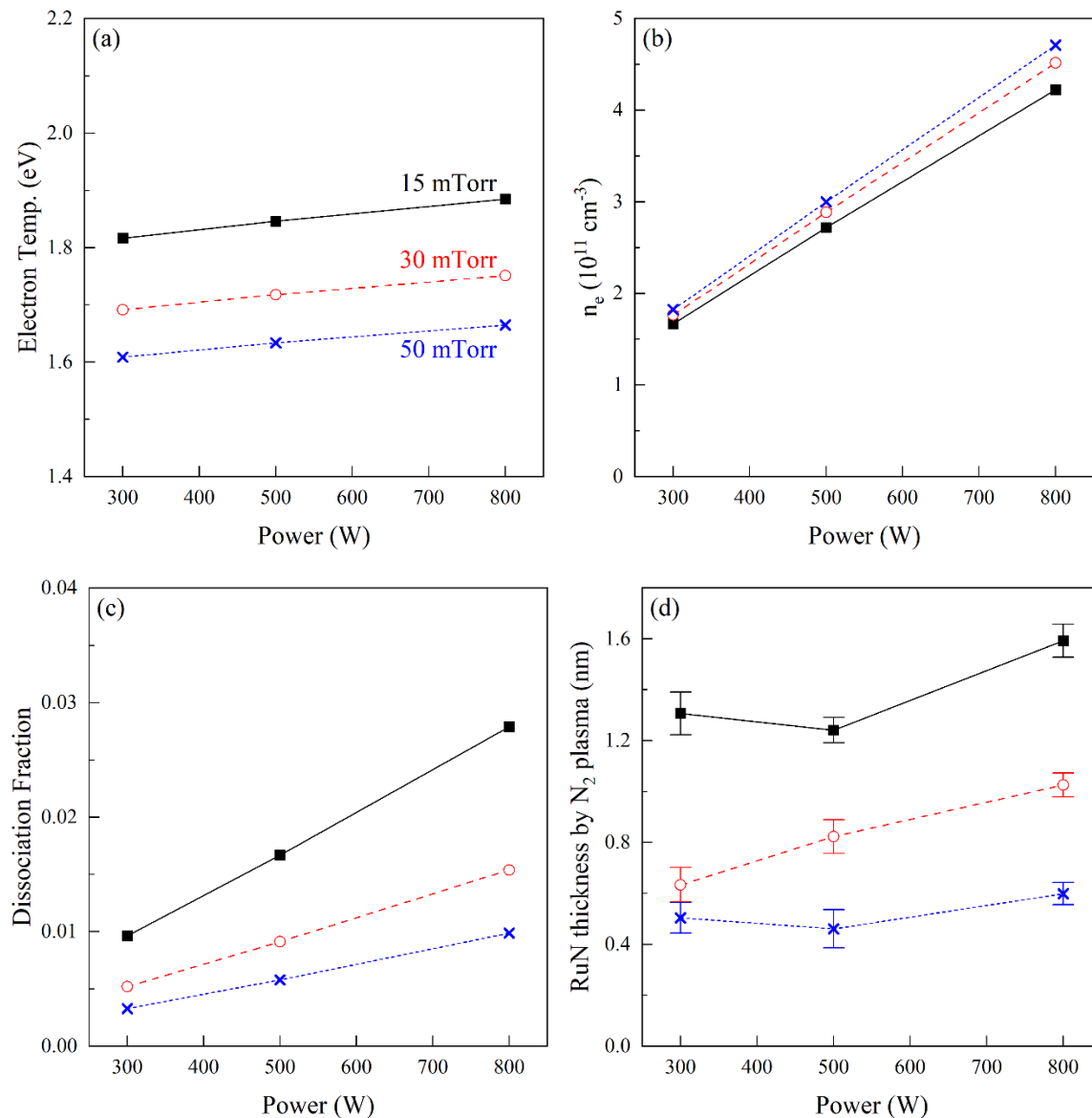


Figure 3.7. Plasma parameters from Chemkin simulation of N_2 plasma. (a) Electron temperature is mainly dependent on pressure, while (b) electron (and ion) density is dependent on power. (c) Dissociation fraction of N_2 is dependent on both power and pressure. (d) Experimentally determined thickness of RuN after plasma nitridation, which correlates best with the dissociation fraction of N_2 , indicating that the concentration of reactive N species limits the nitridation process.

As is the case with O_2 plasma, the presence of ions enhances the effect of the plasma. Since no etching is occurring, the role of the primarily low energy ions is to both penetrate into the film

and damage the surface, encouraging the formation of Ru-N bonds. The lower nitridation rate as the duration of N₂ plasma exposure increases is characteristic of a diffusion-limited process, where Ru or N atoms must diffuse through the RuN film to reach the surface or RuN/Ru interface, respectively, to form new RuN. While the ions can implant deeper into the film, bypassing the diffusion process, when the applied bias is increased, the amount of RuN is only slightly enhanced. The higher energy N ions that reach the surface due to the bias may instead contribute to sputtering of the surface, limiting the thickness of the RuN film.

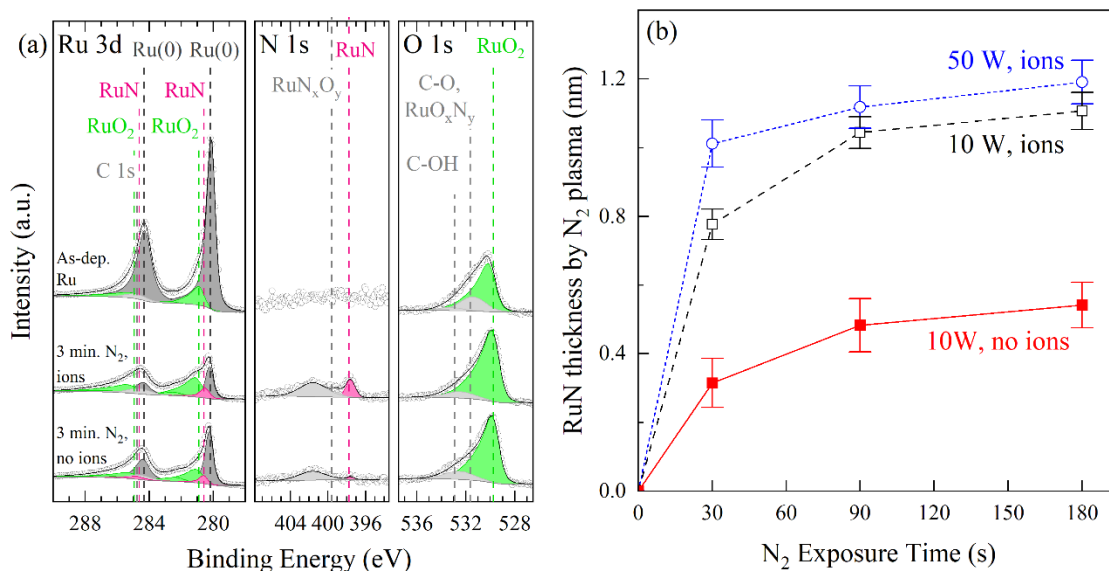


Figure 3.8. (a) X-ray photoelectron spectra of Ru after plasma nitridation with or without ions. (b) The presence of ions results in a greater amount of nitridation, however increasing the bias power does not result in a much thicker RuN layer.

After confirmation that N₂ plasma was able to form a nitride layer on the surface, the passivating properties of the film were examined. After exposure of a Ru film to N₂ plasma for 27 minutes, forming a 1.1 nm thick layer of RuN, the film was exposed to O₂ plasma. Scanning electron microscopy was used to measure the overall thickness of the RuN/Ru film, as well as as-

received Ru film that was etched in parallel to the nitridated film. The surface composition and thickness of the film are shown in Figure 3.9.

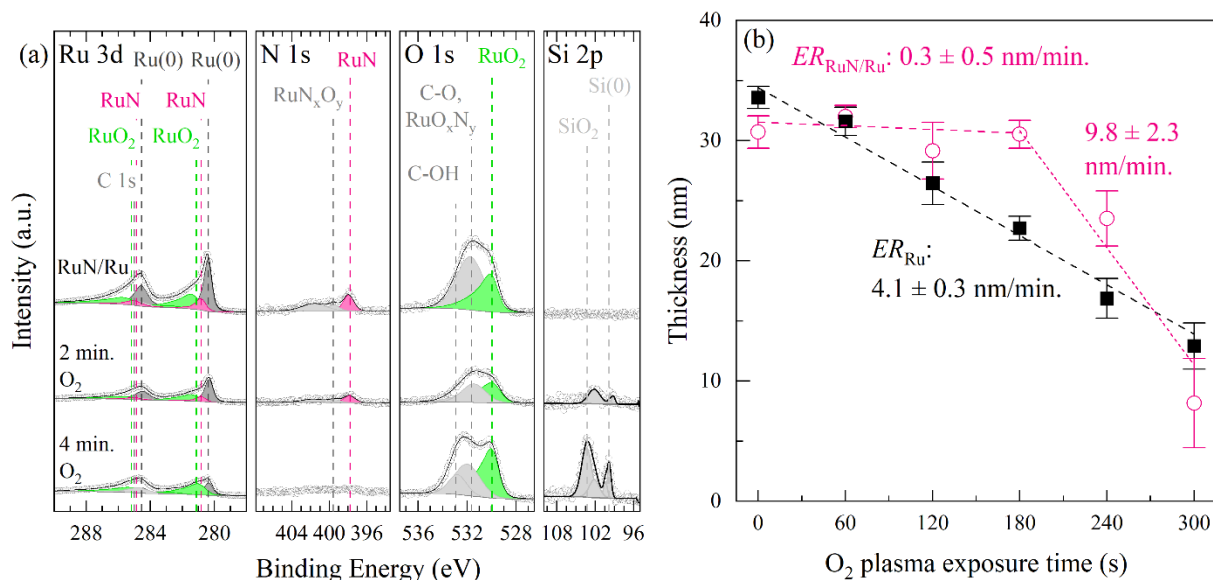


Figure 3.9. (a) X-ray photoelectron spectra of plasma nitridated Ru. After a thin layer of RuN is formed on the surface, subsequent exposure to O₂ plasma causes the RuN layer to oxidize until it is fully removed. (b) Etch rate of nitridated and as-rec. Ru. The RuN layer passivates the surface for the first 3 minutes until it has fully oxidized, then the underlying Ru is etched.

The as-received Ru sample etched continuously, as expected, but the nitridated film did not appear to etch over the first 3 minutes, with a net etch rate of 0.3 nm per minute, which was not significantly different from zero with $p = 0.600$. After this point, the RuN was fully oxidized and etching proceeded as normal. The XPS results from the films show an initial RuN layer that shrinks until it is fully replaced with RuO₂ after 4 minutes. This indicates that the RuN oxidation proceeds at a lower rate than Ru, which means that the further oxidation of RuO₂ to RuO₄, the actual etching reaction, is limited by the formation of RuO₂. After the RuN is fully removed, there is no inhibition of the etching reaction.

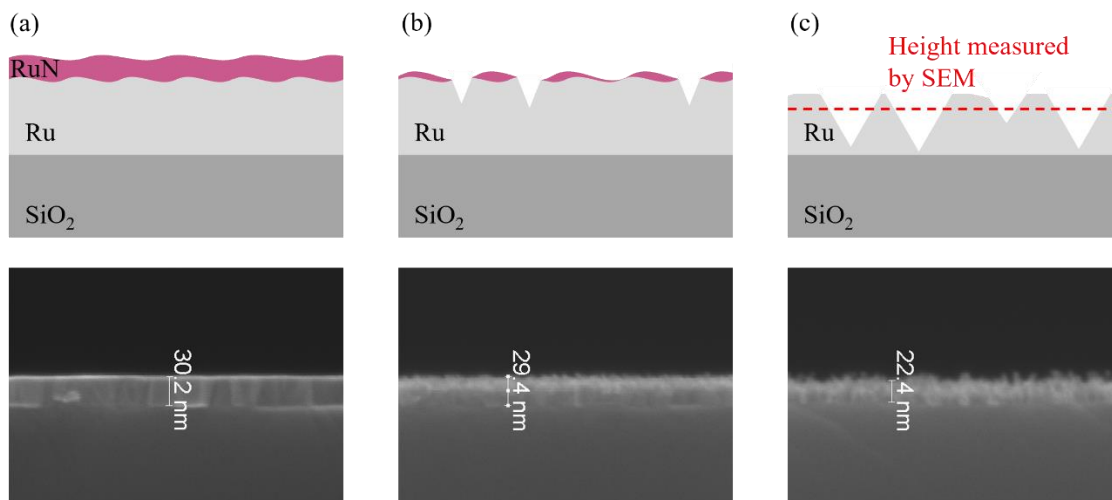


Figure 3.10. Schematics and corresponding SEM images of (a) nitridated Ru after (b) 2 minutes to (c) 4 minutes of exposure to O_2 plasma. As the sample is etched, variations in where the RuN is removed first leads to variations in the underlying Ru thickness. When the sample is measured by SEM, the effective etch rate is higher due to the partial removal of Ru.

The etch rate of the nitridated film is significantly higher than the as-received Ru after the RuN is removed, with a p -value equal to 0.014. Since the underlying Ru should be unaffected by the nitridation process, another mechanism must be found to explain this phenomenon. From Figure 3.9(a), in the XPS of the nitridated Ru after 4 minutes of O_2 plasma exposure, the Si 2p peak corresponding to the underlying SiO_2 layer can be seen. Despite this, the SEM image indicates a thickness of over 20 nm, which is well beyond the escape depth of Si 2p photoelectrons. To resolve this contradiction, the Ru surface must have varying thickness, such that the SEM appears thicker, while Si 2p photoelectrons can still be detected. To explain the variations, then, the thickness or removal rate of the RuN itself must vary, from localized damage by ions, leading to breakthrough of the RuN films at varying times. In the areas where the RuN was removed first, the underlying Ru could be etched, similar to a micromasking effect. When the RuN was fully removed and the bulk of the film was etched, the variation in surface thickness leads to an increased

etch rate as measured by SEM. This occurrence of this indicates that the duration of O₂ plasma must be carefully controlled to prevent breakthrough of the RuN intended to act as a passivation layer.

3.3 Chemical Reduction of RuN with H₂ Plasma

While RuN was shown to be an effective passivation layer, to achieve better control over processes using it, it is necessary to selectively remove it. While organic passivation layers used in other anisotropic processes can be removed by sputtering thanks to the difference in sputtering threshold between the passivation and underlying layers, a chemical approach can be used here to reduce RuN to Ru through the removal of N from the surface. To do this, H₂ plasma has been established as an effective reducing agent, particularly for RuO₂. As RuN is less stable than RuO₂, and Ru-N and Ru-O bonds have similar dissociation energy, H₂ plasma was predicted to be able to reduce Ru. As no volatile RuH_x compound is known, and H is such a light ion, it was not expected to sputter Ru even when a bias is applied. However, the removal of N could be enhanced by ions, which could additionally damage the surface and enhance subsequent oxidative etching of Ru.

The H₂ plasma was first characterized by OES, much like the other plasmas. The well-known Balmer series were seen starting from the $n = 3$ to 2 peak present at 656 nm. While H₂ peaks were faintly visible, the H₂ plasma appeared to be significantly dissociated. Like was the case for N₂ plasma, atomic Ru could not be seen indicating a lack of etching during exposure.

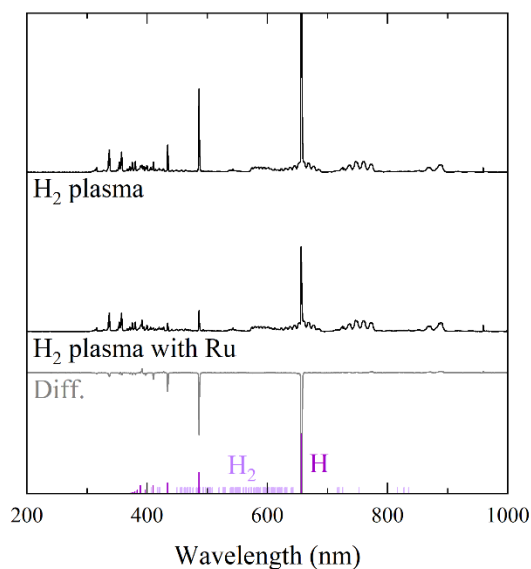


Figure 3.11. Optical emission spectroscopy of H_2 plasma. The difference spectrum between the spectra with and without Ru present in the chamber is shown in gray. The lack of Ru peaks in the spectra indicate that the Ru is not being etched.

The reduction of Ru oxides and nitrides in H_2 plasma was confirmed by exposing bulk RuO_2 and RuN films in Figure 3.12. Since these films were deposited by reactive sputtering, there was no Ru metal layer present before H_2 plasma exposure, ensuring that the Ru metal seen in the XPS was due to reduction, rather than removal of a surface film. Since the films were exposed to air prior to characterization, some native oxide was formed on the surface, but the Ru^0 peaks prove that hydrogen was an effective reductant.

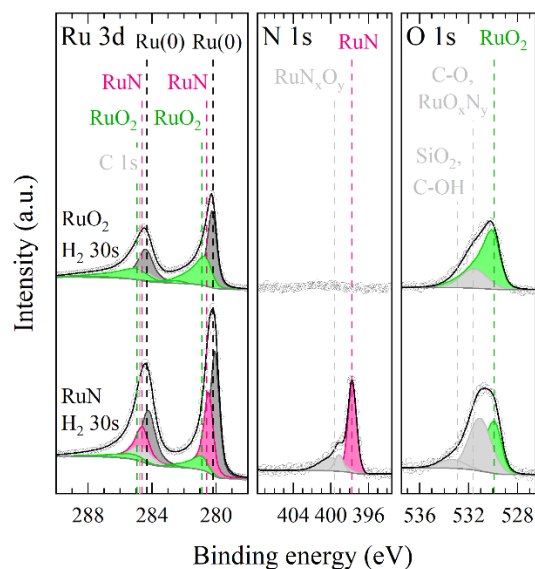


Figure 3.12. X-ray photoelectron spectra of bulk RuO_2 and RuN films exposed to H_2 plasma for 30 seconds. The presence of Ru^0 in the spectra confirms reduction.

The effects of plasma power and pressure on reduction were explored in Figure 3.13, which showed that both pressure and power had a weak relationship with the overall thickness of RuN reduced. This indicates that increased ion density and dissociation fraction do not significantly enhance the reduction, and it is instead limited by diffusion of H .

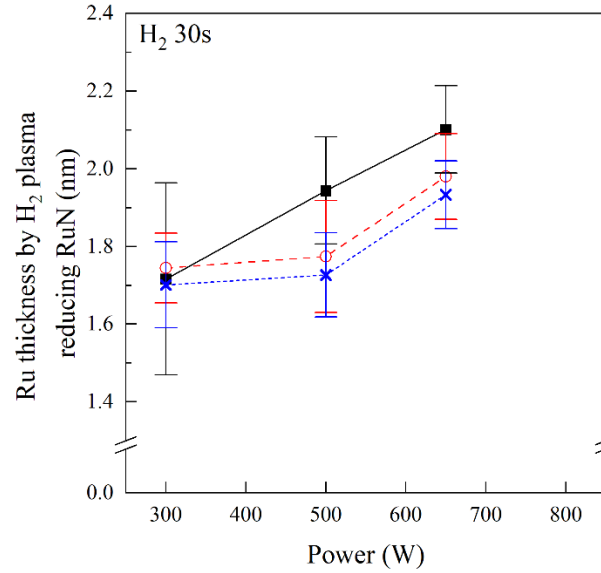


Figure 3.13. Experimentally determined thickness of Ru from the reduction of RuN by H_2 plasma. The thickness is weakly dependent on both power and pressure.

The effect of ions on reduction was similar to nitridation, where ions enable a thicker modified layer, as they penetrate deeper into the film. Interestingly, the high applied bias condition results in a thinner reduced layer than with lower applied bias. This can be explained by physically etching of the RuN at higher bias, as the more energetic H ions are able to remove RuN, leading to a steady-state where the reduction of RuN is balanced by the etching of Ru, leading to no change in the thickness of the reduced layer after 30 seconds of exposure.

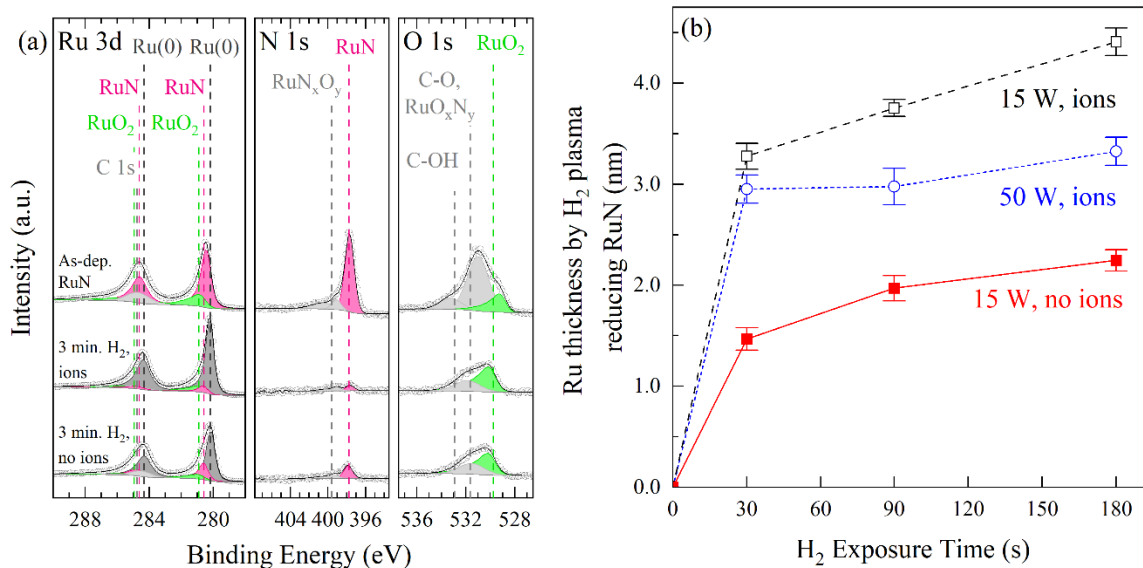


Figure 3.14. (a) X-ray photoelectron spectroscopy of blanket film RuN exposed to H₂ plasma. With and without ions, a layer of Ru is formed as RuN is reduced. (b) Ions enhance the reduction of RuN, reaching deeper into the film and forming a thicker layer of Ru on the surface. When the bias power is high, the thickness of the Ru layer is lower, as etching occurs and the overall thickness of the film is reduced.

The reduction of RuN was performed primarily on bulk RuN films as a baseline, but RuN formed by plasma nitridation was also reduced by the same process.

3.4 Controlling Cyclic Etch of Ru by Ion Exposure

To develop anisotropy, the effect of preventing ions from reaching the surface during exposure of O₂ plasma to nitridated Ru was tested in Figure 3.15(a). Without ions, the film was etched at a rate of 0.6 nm per minute, with a *p*-value of 0.002 indicating that the etch rate was meaningfully different from zero. This reported etch rate was significantly lower (*p* < 0.001) than the baseline etch rate of 2.4 nm per minute of as-deposited Ru without ions that was previously shown in Figure 3.4. Though ions in the unbiased O₂ plasma are unlikely to have energy greater than 20 eV, many have energy sufficient to break Ru-N bonds and damage the surface, which can

promote oxidation. In the absence of ions, the purely chemical oxidation of RuN occurs, but at such a limited rate that no inflection point can be seen. This provides a way to selectively etch at the bottom of a trench while not etching the sidewalls due to the much lower ion flux striking the sidewalls. However, the initial period of passivation still occurs on the ion-exposed samples, and any uneven removal of RuN can lead to surface roughness enhancement.

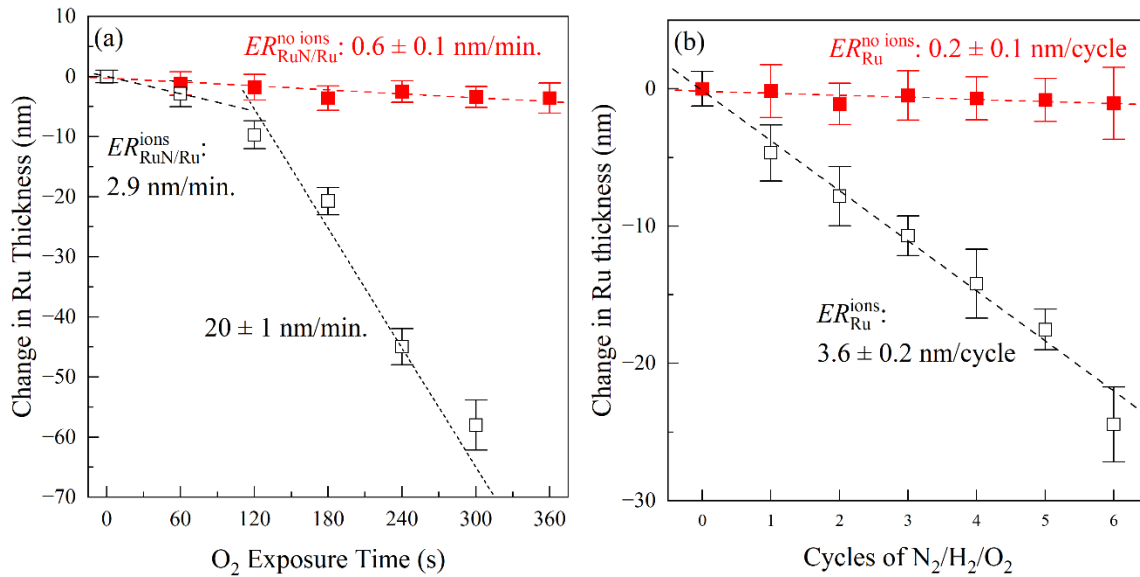


Figure 3.15. Effect of ions on combined processing of Ru films. (a) Nitridated Ru films exposed to O₂ with or without ions. When ions are not present to enhance the etch, the RuN is able to resist oxidative etching for at least 6 minutes. (b) Cyclic N₂/H₂/O₂ plasma etching of Ru. With ions, the process etches Ru consistently. Without ions, the process does not significantly etch as enough RuN remains on the surface to passivate the surface against etching by O radicals.

Having determined the effects of individual N₂, H₂, and O₂ plasma, they were combined into a single cyclic process, which consisted of 30 seconds of N₂ plasma, 5 seconds of H₂ plasma, and 30 seconds of O₂ plasma. The addition of the H₂ plasma step was intended to remove RuN from the surface, while its short duration was meant to prevent complete removal of the RuN from the surface not exposed to ions. The etch rate of the cyclic process was 3.6 nm per cycle with ions

present. Without ions, the etch rate was found to be 0.2 nm per cycle, which was not significantly greater than zero, with $p = 0.062$. While the p -value was close to 0.05, the variance in the measurements from SEM was too great to confirm that etching had occurred. In Figure 3.15(b) the results of this process can be seen, with a ratio of 18 between the condition with and without ions. Compared to the ion/no ion ratio of 4.6 for O_2 plasma alone, the three-step process displays an improvement to the selectivity between conditions that can translate to anisotropy on patterned samples.

To confirm that the cyclic process also improved on the partial etching of Ru, the surface roughness and resistivity of partially etched films was measured as a function of thickness for etching by O_2 plasma or $N_2/H_2/O_2$. Although the roughness of the underlying Ru film was a concern in the case of etching nitridated Ru, in the three-step process, the reduction step ensures that the Ru can be freely etched without a micromasking effect, resulting in a smoother surface. The O_2 plasma, on the other hand, was significantly roughened during etching, with a p -value equal to 0.017 for the difference in the two processes. In addition to roughness induced by ions, RuO_2 promotes the adsorption of O radicals, leading to the formation of RuO_2 islands. This variation in oxidation causes roughness on the surface.

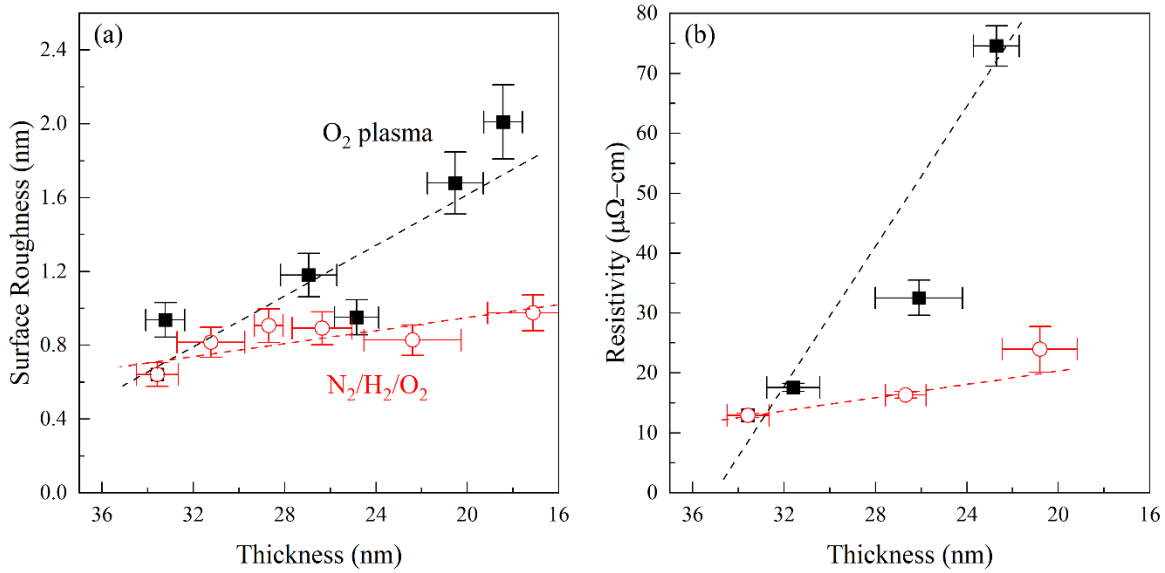


Figure 3.16. (a) Surface roughness and (b) resistivity of blanket Ru films after etching by continuous O₂ plasma or cyclic N₂/H₂/O₂ plasma. For equivalent amount of etching, the cyclic process results in a smoother surface and lower resistivity.

The repeated reduction of the surface during the three-step cyclic process meant that RuO₂ was unable to form as thick a layer, only 2.3 nm compared to 3.5 after pure O₂ plasma. In addition to limiting the roughness formation mechanism, the thinner oxide layer less to less increase in the resistivity after N₂/H₂/O₂ etching. The increase to surface roughness also contributed to the greater resistivity of the O₂-etched sample due to the greater surface interface scattering of electrons, and effectively thinner layer after considering oxidation.

The three-step N₂/H₂/O₂ process demonstrates a greater ion/no ion etch rate ratio, indicating anisotropy on patterned samples, and resulted in less damage to the surface of partially etched films without requiring highly energetic ions or corrosive chemistry, making it suitable for extension to the etching of patterned features for interconnect integration.

Chapter 4. Anisotropic and Selective Etching of Ruthenium

While the results from blanket film studies demonstrated that the addition of surface modification steps to an O₂-plasma-based etch process was able to alter the etch results when ions were blocked from the surface, anisotropy itself must be proven using patterned samples. As the sidewall is exposed to lower ion flux, the passivation of the sidewall predicted from the blanket film results was proven using patterned samples with a variety of scales down to sub 100 nm pitches. To quantify batches of TEM imagery of etched samples, an image processing pipeline was developed to produce line profiles of the Ru features as well as to determine the anisotropy and selectivity of process quantitatively. The role of both N₂ and H₂ plasma in shaping the etch profile of the O₂ plasma was determined, with nitridation resulting in tapering of the etch profile due to protection of the sidewall and edges of the trench, while reduction resulted in the removal of the nitride, allowing more etch in those areas. By using both steps together, the process could be tuned to result in a vertical profile without significant damage to the hard mask, and with improvement to the aspect ratio dependence of the process.

4.1 Confirming Anisotropy of N₂/H₂/O₂ Process

The results on blanket films either shielded or exposed to ions suggested that anisotropy was possible due to the anisotropic distribution of ions. To validate this assumption, studies of ICP plasmas at similar conditions suggest that the full width at half maximum (FWHM) of the ion angular distribution is 4-6° over the range of conditions and chemistries studied (Song et al., 2020; Wen et al., 2017; Zhang et al., 2019). Based on the neutral temperature, electron temperature, and electron density of similar plasmas (Fiebrandt et al., 2017; Kang et al., 2011; Kiehlbauch & Graves, 2003; Krištof et al., 2016; Tonniss & Graves, 2002), the mean free path is two orders of magnitude

greater than the Debye length, indicating that the sheath is largely collisionless, and the ion angular distribution is narrow. In addition, the patterned samples used in this work have aspect ratios of 4 or below.

A rough estimate of the relative ion flux to the trench sidewall or bottom can be found by assuming the ion angular distribution is normal and centered on the surface normal, taken to be 0° . An ion centered at the top of the trench reaches the sidewall if it has an angle greater than $\theta = \tan^{-1}(1/2A)$ where A is the aspect ratio of the trench. Integrating the area of the normal distribution between θ and $-\theta$ results in a probability of the ion striking the bottom of the trench shown in Figure 4.1. In the range of aspect ratios used in this work (<4), the ion flux to the sidewall is minimal compared to the flux to the bottom of the trench. This means that the no ion condition of blanket films can be used as a reference point for the condition on the sidewall of patterned films.

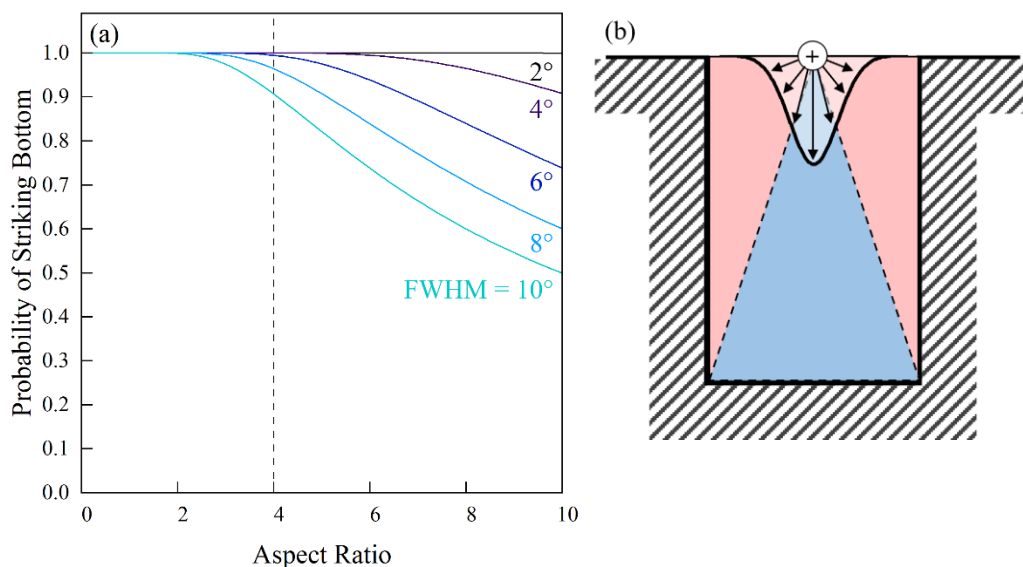


Figure 4.1. (a) Probability of ions with an angular distribution modeled as a normal distribution with FWHM from 2 to 10° striking the bottom of a trench vs. aspect ratio. (b) The probability is solely based on the incoming angle of an ion placed at the center of the entrance to the trench. Since all samples in this work have an aspect ratio of 4 or lower, ion flux to the sidewall is minimal.

The patterned samples from set I were fabricated to serve as the basis for initial experimentation using the $N_2/H_2/O_2$ process. These samples consisted of a SiO_2 hard mask of parallel lines with varying pitch from 2 μm down to 400 nm. While these dimensions were much larger than would be expected for integration of Ru into industrial back-end-of-line processes, they enabled basic confirmation of the anisotropy and selectivity of the three-step process.

Oxygen plasma was used as a baseline, as its etching properties had already been well-studied, and the etch rate of the ion-shielded sample suggested that it would be isotropic. After exposure to O_2 plasma for 18 minutes, the Ru film was completely etched, causing lift-off of the SiO_2 hard masks on all but the largest pitch lines. When the exposure time was reduced to 9 minutes, the Ru film was fully etched in the trench openings, and significant lateral etching had occurred, as seen in Figure 4.2. The vertical etch rate was found to be 10.4 nm per minute using

partially etched samples, while the lateral etch rate was 6 nm per minute, demonstrating the isotropy of the O_2 plasma through the etching of the sidewall by O radicals.

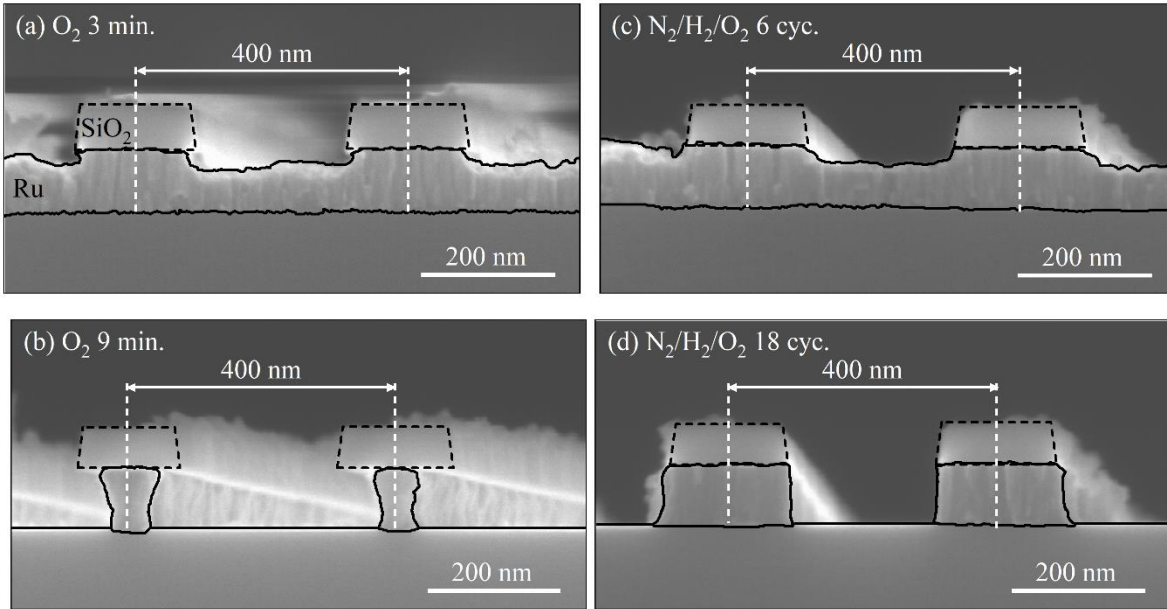


Figure 4.2. Scanning electron microscopy images of 400 nm pitch patterned Ru samples after (a) 3 minutes to (b) 9 minutes of O_2 plasma, or (c) 6 cycles to (d) 18 cycles of $N_2/H_2/O_2$ plasma. The H_2 plasma duration was 15 seconds. The profiles of the Ru and hard mask are outlined to guide the eye. In continuous O_2 plasma, the Ru below the SiO_2 hard mask begins to etch as O radicals attack the sidewall. With the additional N_2 and H_2 plasma steps, the sidewall remains protected even after 18 cycles.

The samples exposed to the $N_2/H_2/O_2$ plasma process, on the other hand, were not etched laterally, resulting in an anisotropic profile with vertical sidewalls. The vertical etch rate of the process was 4.3 nm per cycle, and there was not detectable lateral etching. Sidewall roughness was apparent from some the SEM images, likely stemming from incomplete removal of the photoresist used as a mask for the SiO_2 hard mask opening, which increased the roughness on the hard mask sidewalls, which was transferred to the Ru sidewall, increasing its roughness.

4.2 Quantifying Etch Results with TEM Imagery

To scale the process to sizes closer to those required for the viability of Ru interconnects, samples from set II were exposed to variations of the $N_2/H_2/O_2$ process as well as O_2 plasma only. HRTEM images were processed to generate contour profiles of the Ru features after etching. On these 72 nm pitch samples, 6 to 7 individual Ru features were processed, with representative contours shown in Figure 4.3. The profile of the feature etched by O_2 plasma shows significant undercut, as oxygen radicals chemically etch the Ru sidewall despite the lower ion flux to the sidewall. This result is consistent with the results from ion-shielded blanket films and the larger-pitch patterned samples, where etching was observed even in the absence of oxygen ions.

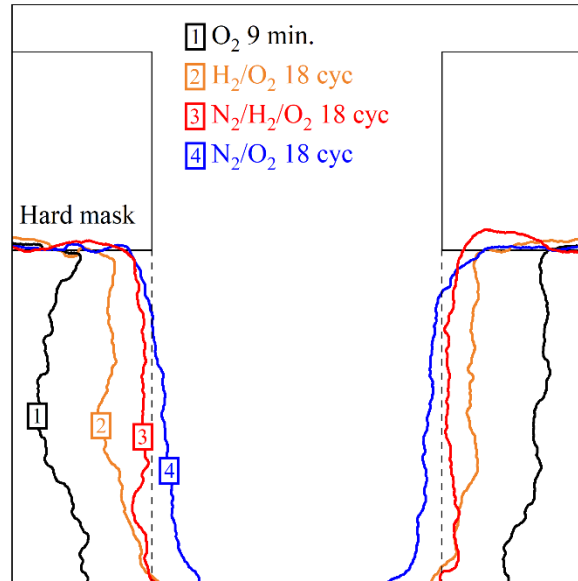


Figure 4.3. Profiles derived from TEM of 72 nm pitch Ru samples. Without nitridation, both the O_2 and H_2/O_2 etched samples were significantly undercut. With the N_2 step, the sidewall is protected from undercut, but the addition of the H_2 step is necessary to prevent tapering at the corners of the trench. The H_2 plasma step duration was 15 seconds.

The addition of the H₂ plasma step to create an H₂/O₂ cyclic process did not prevent lateral etching, as expected. However, a reduction in the amount of lateral etching was observed compared to the baseline O₂ plasma. Since H₂ plasma has been shown to reduce RuO₂ present on the surface of Ru after O₂ plasma etching, the reduction in lateral etch rate can be explained by the reduction of Ru oxides on the sidewall. Since the sidewall etch is primarily radical-driven, the periodic reduction of the sidewall oxide requires re-oxidation before the oxygen radicals can further oxidize it into RuO₄, the volatile etch product. This lowers the lateral etch rate even in the absence of the etch-inhibiting RuN.

When the N₂ and O₂ plasma steps are alternated without the H₂ plasma step, anisotropic etching is achieved. Since RuN is formed during the nitridation step, the etch rate of the sidewall is reduced, with oxygen radicals unable to break through the passivation. Since it is the presence of ions in the O₂ plasma that enables the break-through of the RuN layer, vertical etching is still able to proceed, though at a lower rate. At the corners of the trench RuN inhibits etching, causing the profile to taper. To achieve a vertical sidewall, it was necessary to include both N₂ and H₂ plasma steps. With this N₂/H₂/O₂ process, RuN is formed on all surfaces but is reduced primarily in the surfaces where hydrogen ion flux is high, such as the bottom of the trench. This reduction enhances the etch rate of the O₂ plasma vertically, but the inhibitive effect on the sidewalls due to the presence of RuN remains. This results in a vertical etch profile without tapering, but without significant lateral etching.

To confirm the results of each process step on the surface composition, blanket films samples that were either shielded or exposed to ions were examined by XPS after each step. Since the ion flux is lower to the sidewall, its composition should more closely resemble the composition

of the shielded sample, while the bottom of the trench is exposed to ions. Figure 4.4 shows the effect of each subsequent step of the $N_2/H_2/O_2$ process on the amount of RuN. While more RuN is formed when ions are allowed to reach the sample, the amount of reduction during the plasma step is greater, as well. This results in the sample shielded from ions having a greater amount of RuN after the reduction step, enhancing the selectivity of the etching of the ion-exposed sample over the shielded sample, and equivalently increasing the anisotropy on patterned samples.

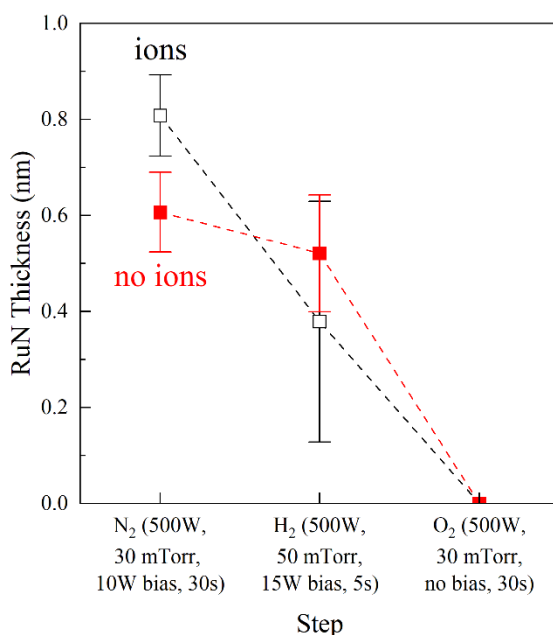


Figure 4.4. Thickness of RuN derived from XPS of Ru samples exposed to two complete cycles of $N_2/H_2/O_2$, then removed after each step of the third cycle. With ion exposure, the extent of nitridation and reduction are both greater in magnitude, resulting a thinner layer of RuN remaining at the start of the O_2 plasma step compared to the sample shielded from ions.

Since the raw TEM imagery was converted into contour profiles, the etch rate of the Ru and hard mask can be measured to determine values of the selectivity and anisotropy of the each process. Finding the change in the Ru or SiO_2 thickness in either the vertical or lateral direction, as depicted in Figure 4.5(a), the etch rates can be determined and used to find metrics to quantify

etching. To define the change in dimensions, the thickness was taken at the thinnest point of the etched film in a particular trench and compared to the thickness of the as-received sample. The width of the features was taken at the thinnest point, and compared to the initial width of the hard mask to determine lateral etch rates. The anisotropy was defined as the ratio of vertical etch rate to lateral etch rate of Ru. An anisotropy of one denotes a perfectly isotropic process, while an infinite anisotropy represents a perfectly anisotropic process. The selectivity of Ru vs. SiO₂ was measured by two metrics: the vertical selectivity, the ratio of vertical etching of Ru vs. SiO₂, and the lateral selectivity, the ratio of vertical etching of Ru vs. lateral etching or deposition of SiO₂. These two values were each critical, as the vertical selectivity is a measure of how thick the hard mask must be to protect the features over the course of the etching process, while the lateral selectivity is a measure of how much the critical dimension of features shifts. Conventional O₂/Cl₂ RIE of Ru results in low vertical and lateral selectivity, as the redeposition of SiO₂ on the feature sidewall shrinks the critical dimensions. Using the TEM profiles of features including the contours shown in Figure 4.4, the values shown in Figure 4.5(b) were determined.

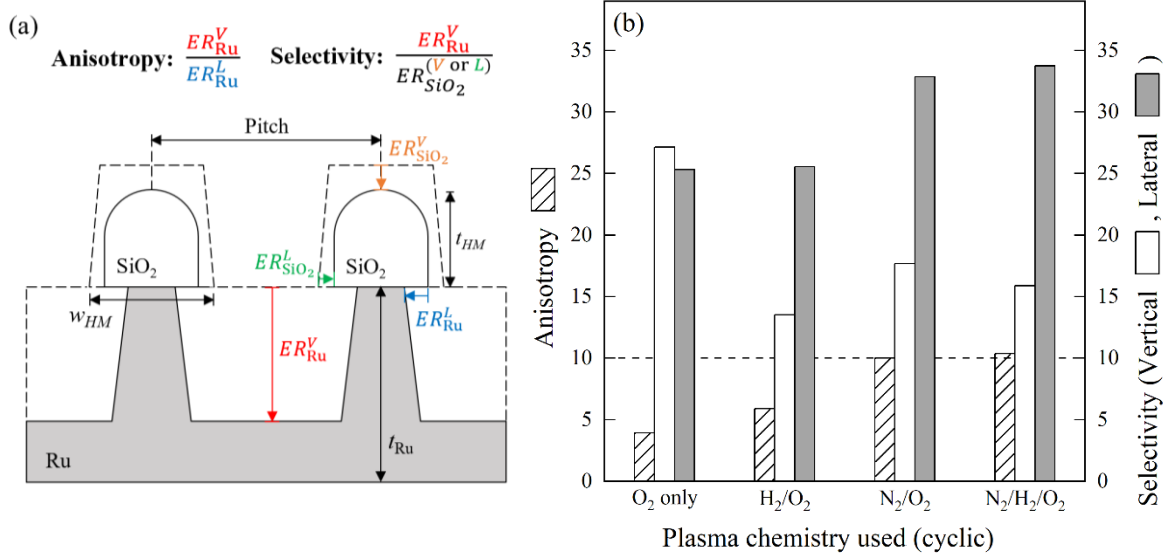


Figure 4.5. (a) Diagram of patterned Ru highlighting etch rate measurements (b) Anisotropy and selectivity of selected processes on 72 nm pitch Ru samples with profiles shown in Figure 4.3. The nitridation step is necessary to improve the anisotropy to above 10. While the addition of N₂ and/or H₂ steps reduces the vertical selectivity, the lateral selectivity of all processes remains above 25.

The baseline O₂ plasma demonstrated an anisotropy of 4.0, as expected from the ratio of ion/no ion etch rate of blanket films in O₂ plasma, which as was 4.6. Since the bottom of the trench was exposed to ions and radicals, while the sidewalls were primarily exposed to radicals only, the vertical etch was higher, but without inhibition, the lateral etch was still significant. The anisotropy of the H₂/O₂ process was 6.1, an increase from O₂ plasma alone. Due to the reduction of the Ru oxide on the sidewall, the purely chemical lateral etching was hindered, but in the vertical direction, the ion-enhanced etch was not as affected, leading to a slight increase in the anisotropy. With the cyclic N₂/O₂ process, the anisotropy was raised to 10. While the tapering of the sidewall meant much of it was not etched at all, compared to the width of the hard mask, slight recessing at the top of the Ru film was reported as a non-zero lateral etch rate. The addition of the H₂ plasma step did not reduce the anisotropy, as the more vertical profile did not have a smaller width relative

to the recessing of the top corners seen after N_2/O_2 etching. In addition, the $\text{N}_2/\text{H}_2/\text{O}_2$ process etched Ru in the vertical direction at a slightly higher rate (2.7 vs. 2.4 nm per cycle), offsetting any increase to the lateral etch rate.

While the O_2 plasma alone was not anisotropic, the lack of applied bias or chemistry to etch the SiO_2 hard mask resulted in vertical and lateral selectivity above 25. Because oxygen is unable to chemically etch SiO_2 , and the energy of the ions in the plasma is likely to be less than 20 eV due to the lack of bias applied during this step, there is little change in the vertical thickness of the hard mask. Similarly, because there is no etching of the hard mask laterally, the hard mask's lateral dimensions do not change. Redeposition is not a factor due to the very low etch rate of the hard masks.

With the addition of the H_2 plasma step, the vertical selectivity is decreased. While the absolute vertical etch rate of the SiO_2 in H_2/O_2 increases from 0.14 to 0.17 nm per cycle, the vertical etch rate of the Ru is lower, resulting in a noticeably lower vertical selectivity, though the lateral selectivity is unchanged. Similarly, though the etch rate of the SiO_2 is unchanged by the addition of N_2 to create the N_2/O_2 and $\text{N}_2/\text{H}_2/\text{O}_2$ processes, the vertical selectivity is slightly reduced due to the lower Ru etch rates compared to O_2 plasma alone. The greater sputtering yield of ions at incident angles of $45 - 70^\circ$ causes some rounding of the hard mask, but does not affect the overall vertical or lateral dimensions significantly. Since any etching of the hard mask is likely to be from physical sputtering redeposition would be expected due to low volatility. However, the overall low rate of etching in all conditions means that no redeposition was seen.

Extending the processes to samples from set III, with a sub-10 nm opening was necessary to further confirm the properties of the etching process at scales where Ru interconnects are

relevant. The effects of O_2 , H_2/O_2 , and N_2/O_2 on these smaller dimension and higher aspect ratio samples is shown in Figure 4.6(a). The O_2 plasma and H_2/O_2 etched profiles show lateral etching, with anisotropies of 6.7 and 5.7, respectively. Due to the higher aspect ratio, the ion to radical flux ratio should be higher, so less radicals are available to etch laterally, raising the anisotropy slightly compared to the 72 pitch samples. The tapering effect of the N_2/O_2 was exaggerated compared to the 72 nm pitch samples, with the vertical etch rate being significantly reduced, and the anisotropy becoming effectively infinite. Like the other steps, decreased radical flux, and even ion flux to the corners of the trench likely led to more effective inhibition of the etching process by RuN, leading to tapering, which was increased by the lower fluxes reaching the bottom of the higher aspect ratio structures.

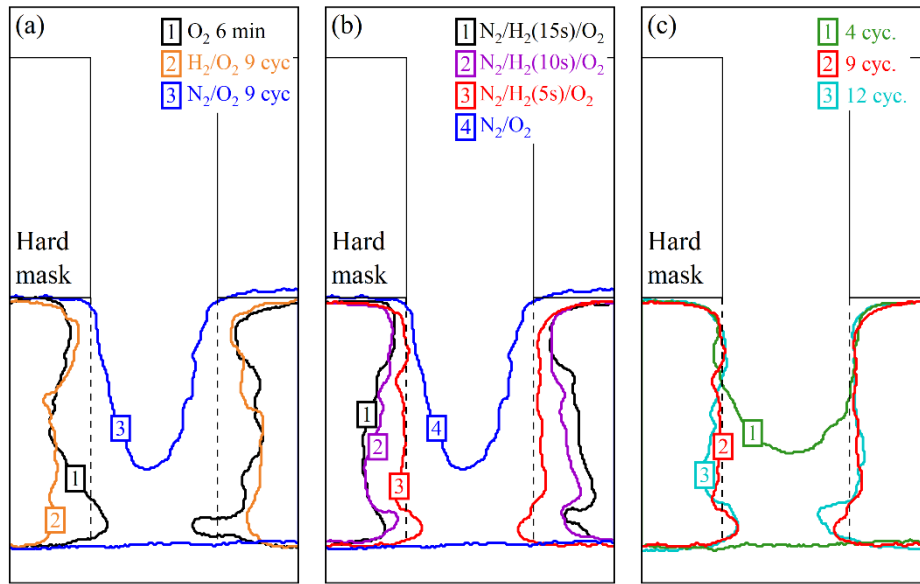


Figure 4.6. Profiles derived from TEM of patterned Ru samples with 10 nm openings. (a) Effect of adding N_2 or H_2 step to O_2 plasma etch. Nitridation prevents undercut but leads to significant tapering at this scale. (b) Effect of H_2 plasma step time on the profile. Reducing the duration of the H_2 step reduces undercut without reintroducing tapering. (c) Effect of cycles of $N_2/H_2(5s)/O_2$ on the profile. Over-etching has little effect on the profile.

When the $\text{N}_2/\text{H}_2/\text{O}_2$ process was performed on the smaller samples, the anisotropy seen at larger scales was lost. This was likely due to changes in the ion to radical flux ratio and may be dependent on the different conditions during each plasma, such that the amount of RuN formed is lower, while the reduction during the H_2 plasma step is less affected by the increased aspect ratio. To ameliorate the loss of anisotropy that was caused by the H_2 plasma step, the duration of the step was reduced, as is shown in Figure 4.6(b) as well as in Figure 4.7. As the hydrogen duration was reduced, the anisotropy was increased from the baseline of the H_2/O_2 step, representing the case where no RuN remained on the sidewall. When the duration of the H_2 step was lowered to only 5 seconds, the anisotropy was raised to 19, while the profile was vertical, as can be seen visually. To confirm that this sidewall passivation was consistent, and over-etching would not lead to damage, additional cycles were run as shown in Figure 4.6(c). As the number of cycles increases, the previously-exposed sidewall is not damaged, indicating that the process is anisotropic and not sensitive to overetching.

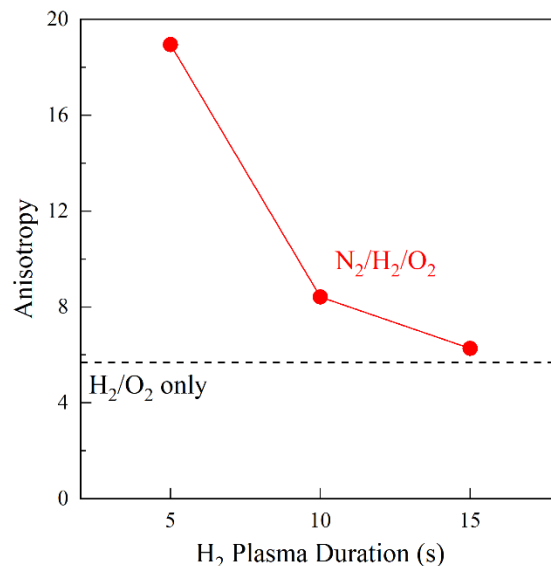


Figure 4.7. Anisotropy of the N₂/H₂/O₂ process on 18 nm pitch samples as a function of the H₂ step duration, compared to the anisotropy of the H₂/O₂ process. While 15 seconds of H₂ plasma did not impact the anisotropy of the larger pitch samples, here it is necessary to reduce the duration to regain anisotropy.

To further examine the effects of aspect ratio and the resultant changes in flux of reactive species, a series of features with aspect ratios ranging from 1.3 to 3.9 were etched by O₂ plasma or the N₂/H₂/O₂ process. In Figure 4.8, the effects of aspect ratio on etch rate can be seen. The etch rate of Ru in O₂ plasma was shown to have a high dependence on the aspect ratio, with complete etch through of the 16 nm Ru film occurring on the 1.3 AR features, while only half the film was etched in the 3.9 AR trenches. On the other hand, the cyclic process was less sensitive to the aspect ratio. In the case of O₂ plasma, the reduced radical flux to the trench may lower the overall etch rate. However, in the N₂/H₂/O₂ plasma, lower radical flux may lead to less RuN being formed, while the ion-enhanced hydrogen reduction is able to reduce more of it, leading to the etch rate of the N₂/H₂/O₂ process being similar to the etch rate of the O₂ plasma process at higher aspect ratios.

At lower aspect ratios, more RuN would remain, lowering the etch rate of the cyclic process relative to O₂ plasma alone.

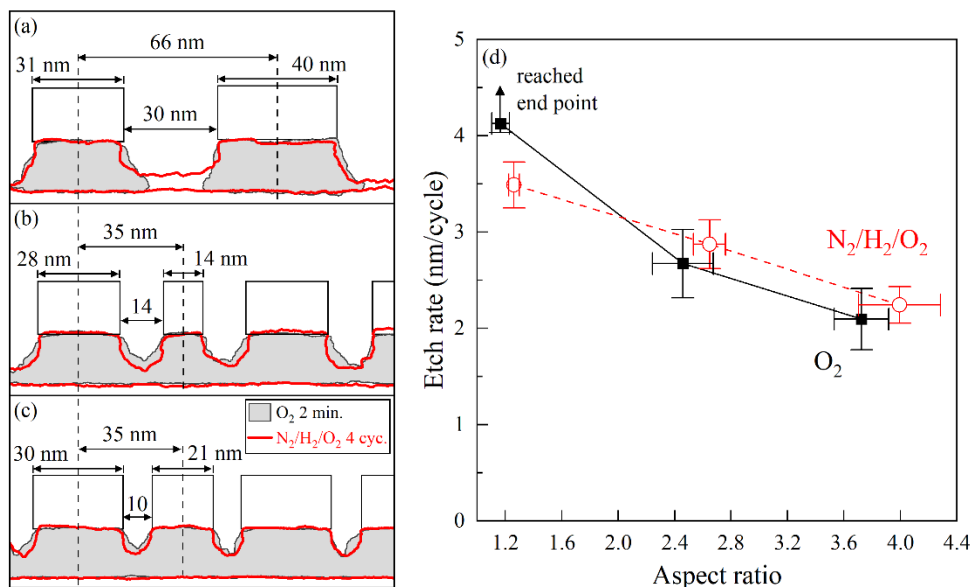


Figure 4.8. Profile of samples etched by O₂ plasma or N₂/H₂(5s)/O₂ with aspect ratios of (a) 1.2, (b) 2.4, or (c) 3.8. (d) The etch rate of N₂/H₂/O₂ is less dependent on the aspect ratio compared to continuous O₂ plasma.

By examining the effects of the N₂/H₂/O₂ process as well as its constituent steps on patterned samples, it was determined to be both selective and anisotropic. The RuN etch inhibition mechanism seen on blanket film samples shielded from ions was shown to occur on the sidewalls of patterned Ru samples, leading to high anisotropy, while the low applied biases and chemistry that is nonreactive to SiO₂ led to high selectivity. The effect of aspect ratio on ion and radical flux was shown to affect the etching characteristics of the plasmas, with smaller higher aspect ratio structure requiring less H₂ plasma to prevent complete removal of RuN on the sidewall, but in turn the cyclic process etch rate was less dependent on aspect ratio compared to the baseline O₂ plasma.

Chapter 5. Compositionally Controlled Etching of CoFeB

Etching of CoFeB was achieved through the combination of a surface modifying plasma oxidation step followed by exposure to either formic acid vapor or hexafluoroacetylacetone vapor. The process was selective to Fe over Co, as was observed in etching of the elemental metal films, as well as through enrichment of Co during etching of CoFeB. The plasma oxidation process was shown to oxidize Co into Co_3O_4 , which could hinder etching by preventing reactions to form Co (II) products, lowering the etch rate of Fe. While greater enrichment of Co was seen when hfac was used as the etchant vapor, the overall etch rate was 0.55 nm per cycle, twice as high as the etch rate of O_2 plasma and formic acid vapor at equivalent conditions, 0.26 nm per cycle. Increasing the temperature of the formic-acid-based process to 120°C increased the etch rate to 0.33 nm per cycle, but raising the pressure to 350 Torr reduced the etch rate to 0.16 nm per cycle.

5.1 Solution Phase Etch of Co, Fe, and CoFeB

To assess the etching of CoFeB and its constituent elemental metals in organic acids, solution phase processing was performed to serve as a baseline for the reactivity of each metal and organic species. To match the proposed vapor phase conditions, the solutions were heated to 80°C . To reduce the etch rate, the solutions were diluted to 1% in deionized water. Water alone was not found to etch or modify the surfaces of Co, Fe, or CoFeB. Samples of Co, Fe, and CoFeB were exposed to formic acid as shown in Figure 5.1(a). The etch rate of Fe was higher than Co, and the etch rate of CoFeB samples with an initial composition of 20:60:20 was between that of Co and Fe. After partial etching of the CoFeB, the etch rate was lower as the last 30-40 nm was etched, though it was still higher than the etch rate of pure Co with an overall value of 2.7 nm of CoFeB vs. 0.8 nm of Co per second.

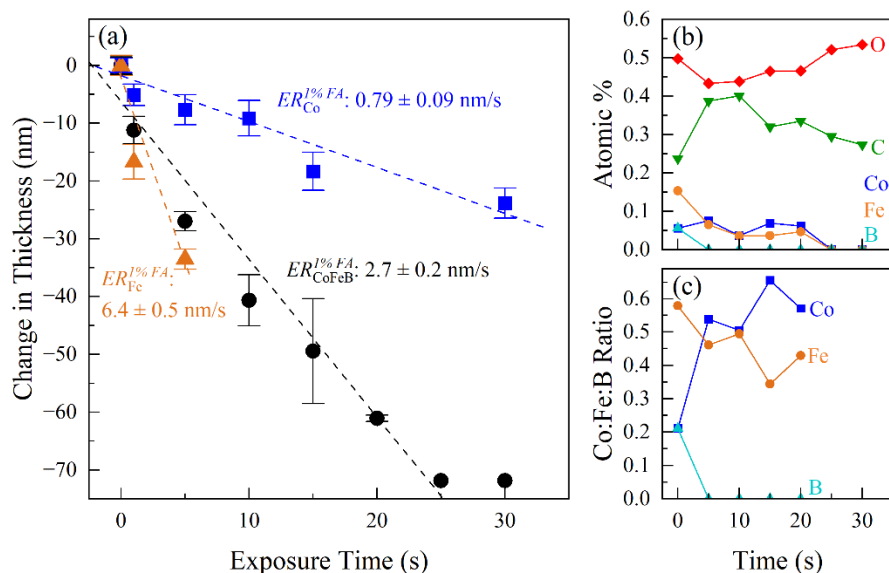


Figure 5.1. (a) Etch rates of Co, Fe, and CoFeB blanket films in 1% formic acid solution. Co etches at a lower rate than either Fe or CoFeB. The etch rate of the CoFeB is reduced over the course of the etch, corresponding with an increase to the amount of Co present on the surface, as seen by XPS in (b) the atomic percentage and (c) Co:Fe:B ratio of the CoFeB film.

The composition of the CoFeB sample surface was measured as a function of formic acid solution exposure time, and is displayed as the overall atomic composition including carbon and oxygen in Figure 5.1(b) and as the Co:Fe:B ratio in Figure 5.1(c). The amount of Co present relative to Fe greatly increased after 5 seconds, while no B was present on any of the etched samples. This was likely due to the formation of boric acid, depleting B from the surface, while the etching of Co and Fe proceeded at a lower rate. The changes in the CoFeB etch rate as etching progressed can be attributed to the difference in etch rate between Co and Fe. With the Fe etching at a higher rate, it is depleted from the surface, resulting in higher Co content on the surface. This reduces the etch rate, and the higher Co content on the surface is maintained as etching proceeds.

The boiling point (70°C) and increased toxicity of hexafluoroacetylacetone (hfac) meant that testing the solution phase etching of CoFeB was not feasible. The etch rate of acetylacetone

(acac), a similar compound with terminal methyl groups instead of $-\text{CF}_3$ groups was measured and compared to the etch rate of CoFeB in formic acid. The selectivity of the etching of CoFeB was determined vs. the etch rate of W, as it is used as a hard mask, and as the underlying electrode layer in some magnetic tunnel junction stacks. The etch rate of CoFeB by formic acid was 251 nm per minute, while the etch rate in acac was only 25 nm per minute, as shown in Figure 5.2.

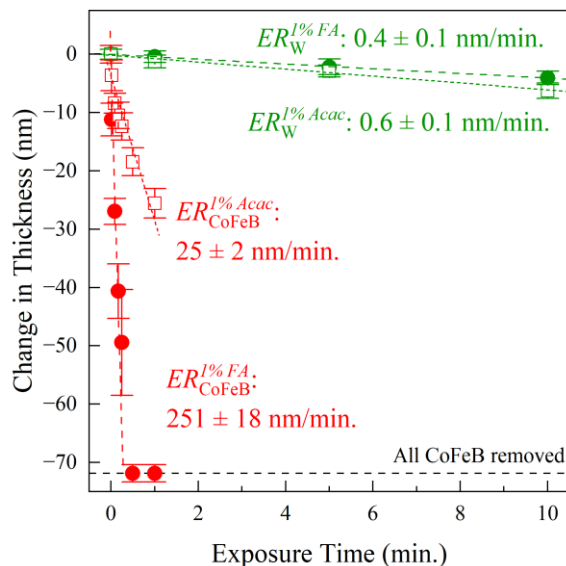


Figure 5.2. Etch rates of CoFeB and W in 1% solutions of formic acid or acac. The CoFeB vs. W selectivity is >400 in formic acid, and 42 in acac.

The selectivity of CoFeB vs. W was very high in both formic acid and acac solutions due to the low etch rate of W. While acac and formic acid form complexes with metals in the +2 or +3 states, the higher oxidation state of W oxide, +6, causes the formation of $\text{W}(\text{COOH})_6$ or $\text{W}(\text{acac})_6$ to not be favorable due to steric hindrance, as has been observed for +4 oxidation state oxides, such as SiO_2 and ZrO_2 (Lee, Noh, et al., 2025).

The solution phase results cannot directly translate to vapor phase results, as the transport adsorption, and desorption of reactants and products differ in the gas phase. The relative etch rates

and surface composition of CoFeB and W after exposure to formic acid and acac demonstrate that organic acid etching is possible, and has high selectivity.

5.2 Vapor Phase Etch of Co and Fe by O₂ Plasma and Formic Acid

To test of the efficacy of formic acid vapor in etching Fe and Co vs. their oxides, samples were exposed to varying amounts of formic acid vapor with or without prior oxidation in 1 minute of O₂ plasma (500W, 35 mTorr, no bias). The results for Fe are shown in Figure 5.3, while the results for Co are shown in Figure 5.4.

The Fe samples were etched at a similar rate with or without prior oxidation, which may be in part due to oxidation in ambient, as the Fe surfaces were found to be primarily Fe₂O₃ with or without oxidation. After exposure of up to 5 minutes of formic acid vapor, up to 2 nm of etching was observed. After further vapor exposure, only the plasma oxidized sample continued to etch. Instead, the unoxidized sample thickness increased from that point on, indicating deposition was occurring. From the composition of the samples surfaces after etching shown in Figure 5.3(b) and (c), the amount of carbon present on the unoxidized Fe surface greatly increased after formic acid exposure, while the amount on the oxidized sample remained roughly constant. While some carbon is expected to appear on the surface due to ambient exposure resulting in adventitious carbon buildup, the large increase seen by only the unoxidized sample in combination with the increase to the film thickness indicates that the formic acid decomposed on the surface, forming an organic contamination layer.

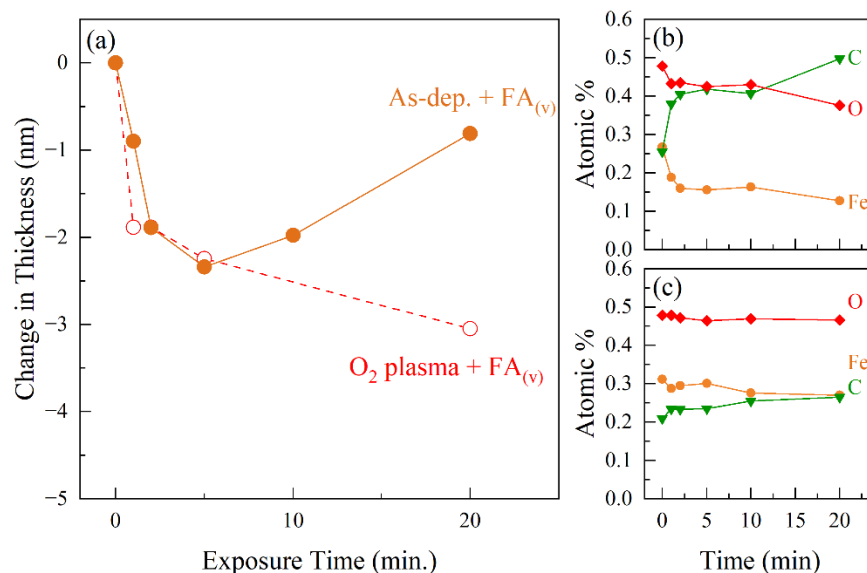


Figure 5.3. (a) Etch of Fe in formic acid at 80°C and 350 Torr as a function of vapor exposure time with and without a prior 5 min. plasma oxidation step. Composition of (b) Fe or (c) plasma oxidized Fe after formic acid vapor exposure. After 10 or more minutes, the thickness of the as-dep. Fe increases, corresponding to a greater amount of carbon on the surface.

On the Co surface, a similar effect can be seen in Figure 5.4(a), where the thickness of the unoxidized as-deposited sample increased as the exposure time increases above 10 minutes, while the oxidized sample continued to etch. The composition of each Co sample surface also followed a similar pattern, where the amount of carbon present on the oxidized sample did not increase after formic acid vapor exposure. While the overall trends are similar between Co and Fe, the amount of etching is different for each metal. After 20 minutes of etching, the oxidized Fe sample was etched over 3 nm, while the Co sample was only etched 1.6 nm. This observation agrees with the solution phase results, where the etch rate of Co was lower than Fe, and enrichment of Co in CoFeB samples was seen. While both Fe samples etched at about the same rate initially, the oxidized Co etched at a lower rate than the as-deposited Co. In the XPS spectra of Co samples, the shape of the oxidized signal in the Co 2p region shifted, indicating that it was oxidized from CoO to Co₃O₄, a

mixed valence oxide containing Co in the +2 and +3 oxidation state. The lower amount of etching of Co_3O_4 compared to the primarily CoO unoxidized surface suggests that Co is more easily etched to form bidentate complexes with organic ligands, while the etching of Co_3O_4 may require a reductive process to convert Co (III) into Co (II), as has been observed using acac as the organic etchant (Partridge et al., 2023).

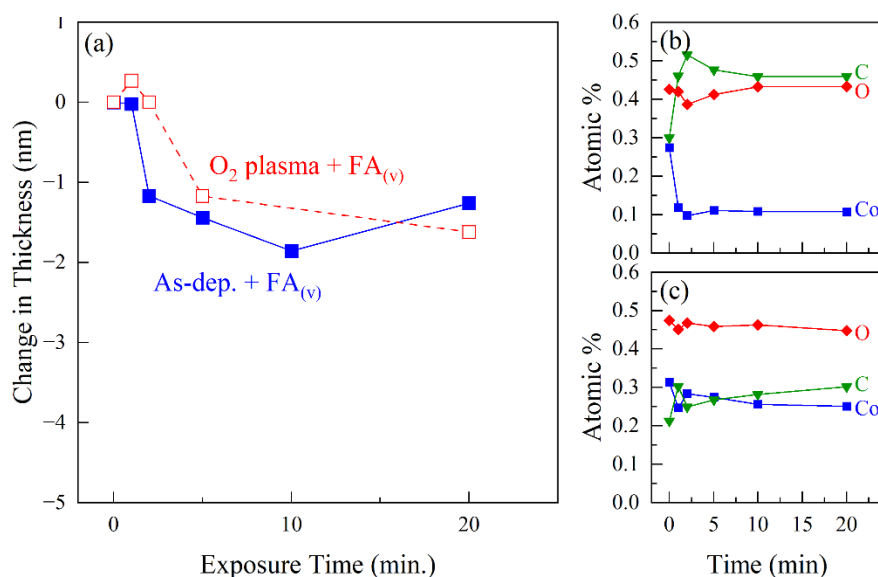


Figure 5.4. (a) Etch of Co in formic acid at 80°C and 350 Torr as a function of vapor exposure time with and without a prior 5 min. plasma oxidation step. Composition of (b) Co or (c) plasma oxidized Co after formic acid vapor exposure. As was the case with Fe, there is a significant increase to the amount of carbon present on the surface of the as-dep. sample.

A cyclic process with alternating cycles of O_2 plasma and formic acid vapor was used to etch the Co, Fe, and CoFeB films. While formic acid vapor was able to etch the as-deposited samples without prior oxidation, to extend the etching process oxidation was necessary to remove organic contamination on the surface and to oxidize metal below the initial native oxide layer.

Etching of the Fe samples with the cyclic O₂ plasma/formic acid vapor process resulted in an etch rate of only 0.14 nm per cycle, as is shown in Figure 5.5(a). The amount of Fe etched was low compared to the single cycle results from Figure 5.3, but the multiple cycles of oxidation may have caused some film expansion as oxygen is incorporated into the lattice. When the temperature of the vapor was raised to 120°C, the etch rate of Fe increased to 0.48 nm per cycle. This increase is attributed to an increased reaction rate for the ligand exchange process, as well as improved volatility of the product species. While formic acid is unstable even at low temperatures, any increase in the amount of decomposition was not reflected in the etch rate of Fe.

The etching of Co by the cyclic process at 80°C was also explored in Figure 5.5(b). Unlike the Fe sample, significant organic film deposition was observed. Since the Co and Fe samples were run at the same time, the cause is unlikely to be due to variation in environmental conditions or contamination of the etching chamber. Instead, the Co etch products may be less volatile and/or more prone to decomposition on the surface, possibly with Co acting as a catalyst that enhances the decomposition, explaining why similar organic contamination is not seen on Fe. The composition of the surfaces after etching confirms the observations from SEM imagery, with the amount of carbon present on the Fe surface remaining roughly constant, while it increased greatly on the Co surface.

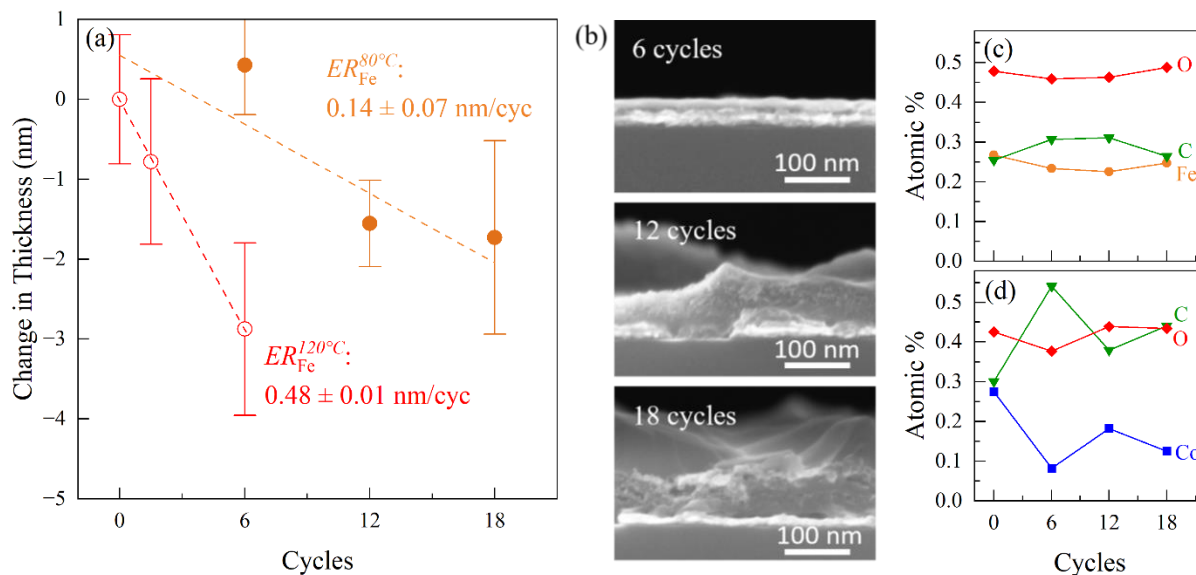


Figure 5.5. (a) Etch rate of Fe over multiple cycles of O₂/formic acid vapor at 350 Torr for 5 minutes, and varying vapor temperatures. Increasing the temperature results in a threefold increase in the etch rate. (b) SEM imagery of Co after cycles of O₂/formic acid at 350 Torr and 80°C. Build-up of organic material on the surface prevented etching. Composition of (c) Fe and (d) Co after cycles with vapor at 80°C. The amount of carbon on the Co surface greatly increases.

To examine the effects of formic acid vapor exposure to Co, samples were measured by XPS after vapor exposure at varying temperatures to either as-deposited or plasma oxidized Co. The difference in oxide peak shape corresponding to Co₃O₄ in the oxidized samples, and to CoO in the unoxidized samples can be seen, with the mixed valence oxide having a sharper primary peak and weaker satellite peak heights. A large peak at 529.5 eV in the O 1s region can also be observed. In the C 1s region, the peak at 288.9 eV corresponds to carbon bonded to two oxygen atoms, the configuration of the carbon atom in a formic acid molecule. This peak appears larger in the samples with CoO on the surface.

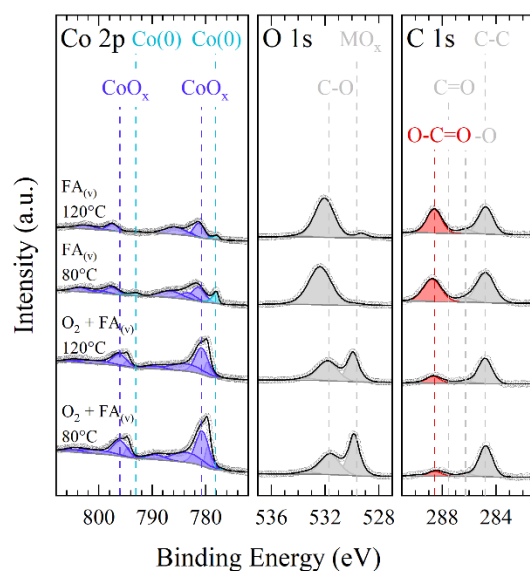


Figure 5.6. XPS spectra of Co after formic acid vapor exposure at varying temperatures with and without prior oxidation. With oxidation, Co_3O_4 is present on the surface, while without oxidation, some metal Co^0 appears in the spectra. The presence of Co in a +2 oxidation state along with O-C=O peaks present in the C 1s and O 1s spectra may indicate the presence of $\text{Co}(\text{COOH})_2$ on the surface. However, on the Co_3O_4 surface, those peaks are less pronounced.

These results indicate that there are two issues with etching Co: firstly, the mixed valence Co_3O_4 is less susceptible to etching in formic acid, as suggested by the relative etch rates of the two Co samples in Figure 5.4(a) and the lack of O-C=O signal in the C 1s region in Figure 5.6. Secondly, the presence of large amounts of carbon on the surface, even on CoO , indicates that the $\text{Co}(\text{COOH})_2$ product is not as volatile as the corresponding Fe etch products, and that the Co surface may catalyze decomposition of organic species on the surface.

5.3 Atomic Layer Etching of CoFeB by O_2 Plasma and Organic Acids

The results in the solution phase with CoFeB, and in the vapor phase with Co and Fe indicate that CoFeB can be etched in the vapor phase, but the presence of Co in the alloy may hinder the overall etch rate or cause etch-blocking organic residues to form. As a baseline

examination of the state of the CoFeB surface after O₂ plasma and/or formic acid vapor exposure, samples were measured by XPS in Figure 5.7. CoO was oxidized into Co₃O₄, though the Fe and B appeared to remain in the +3 oxidation state before and after oxidation. As was the case in pure Co films, the greatest amount of carbon was present on the sample that was exposed to formic acid without oxidation.

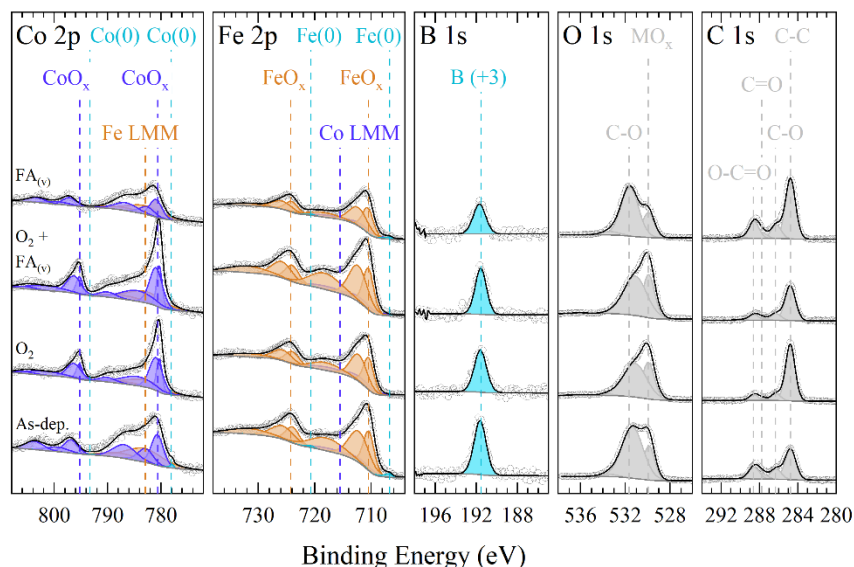


Figure 5.7. XPS spectra of CoFeB after exposure to O₂ plasma and/or formic acid vapor. In all cases, the surface is significantly oxidized, and after O₂ plasma exposure, Co has been oxidized to Co₃O₄.

To determine if the pressure or temperature had an effect on the etch rate, three processes were run with varying conditions during the formic acid vapor exposure step as seen in Figure 5.8. Increasing the temperature to 120°C was found to raise the overall etch rate to 0.33 nm per cycle. The etch rate of the samples at 80°C and either 150 or 350 Torr was 0.26 or 0.16 nm per cycle, respectively. Because of the margin of error in the measured etch rate of the CoFeB after each process, the difference between the etch rates was not significant. In particular, the *p*-value of increasing the pressure from 150 to 350 Torr at 80°C was equal to 0.181, while it was 0.130 when

increasing the temperature from 80 to 120°C at 350 Torr. This indicates that increasing the pressure or temperature did not necessarily lead to an increase in the etch rate, and the etch rate may be limited by the degradation of formic acid on the surface. On the other hand, the effect of temperature on the etch rate of Fe in O₂ plasma and formic acid vapor shown in Figure 5.5(a) was definitively significant with $p < 0.001$. When comparing the etching of Co, where an organic film formed on the surface, this indicates that there is an inhibiting effect when Co is present that limits the etch rate even as temperature is varied.

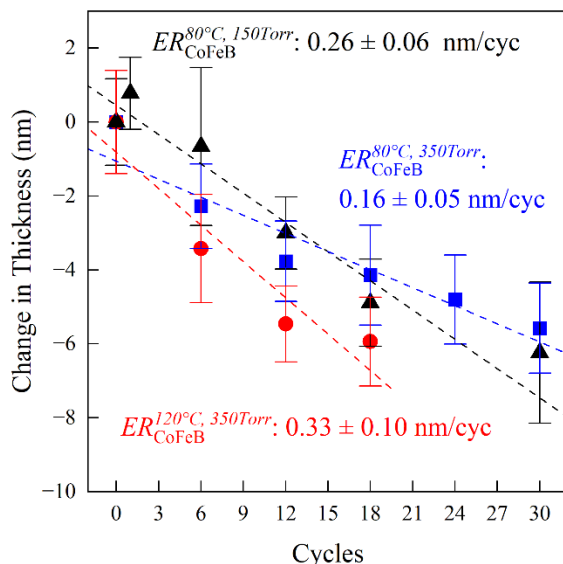


Figure 5.8. Etch rates of CoFeB in O₂ plasma/formic acid vapor. The vapor exposure was performed for 5 minutes with varying pressure and temperature. Increasing the pressure or temperature was not found to have a significant effect on the etch rate.

In all three sets of data, the etch rate is highest at first, but is reduced as the etch progresses. This can be attributed to enrichment of the Co on the surface as etching occurs, as was seen in the solution phase. The surface composition of the CoFeB samples exposed to the cyclic process with vapor at 150 Torr and 80°C is shown in Figure 5.9(b) and (c). The amount of Co on the surface

increases over the course of the etch. The CoFeB was processed at the same time as a W sample to determine the selectivity of the O₂/formic acid process with respect to the two films. After as much as 18 cycles, the thickness of W did not significantly change, with $p = 0.769$ indicating there was no etching of W, giving an effectively infinite selectivity.

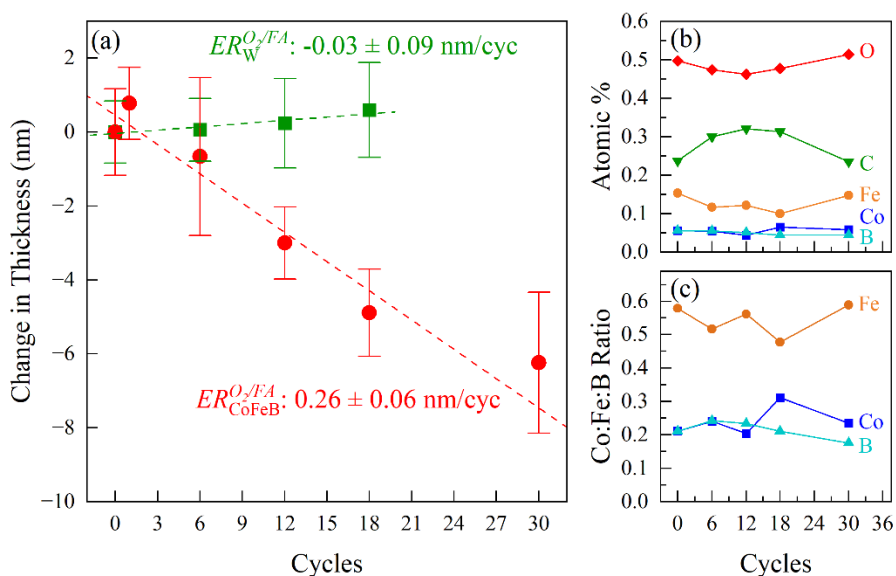


Figure 5.9. (a) Etch rates of CoFeB and W in O₂ plasma/formic acid vapor at 150 Torr and 80°C for 5 minutes. The selectivity of CoFeB vs. W is effectively infinite due to the lack of W etching. (b) Composition and (c) Co:Fe:B ratio of CoFeB after etching. Some Co enrichment can be seen.

With the low etch rates and enrichment of Co seen after exposure to formic acid vapor, other organic acids could potentially replace it. While acac was already seen to have a reduced etch rate in the solution phase, hexafluoroacetylacetone, another beta diketonate with CF₃ groups replacing the CH₃ groups of acac, was predicted to form more volatile compounds with metals, as was reported in Table 1.1. The process used in Figure 5.9 was repeated for the results of Figure 5.10, with the formic acid vapor step replaced with hfac vapor exposure at the same conditions.

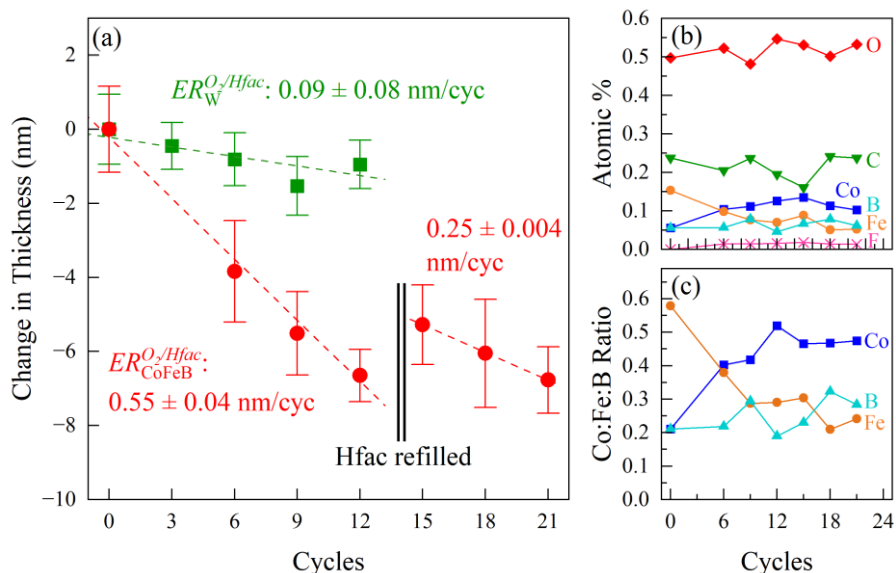


Figure 5.10. (a) Etch rates of CoFeB and W in O_2 plasma/hexafluoroacetylacetone. The selectivity of CoFeB over W is 6 over the first 12 cycles. At 15 cycles, the hfac in the system was depleted and fresh hfac was added. (b) Composition and (c) Co:Fe:B ratio of CoFeB after etching. The amount of Co present on the surface is significantly increased after etching.

The etch rate of the Hfac-based process was twice that of formic acid at the same conditions, confirming that hfac compounds were indeed more volatile and reactive than the equivalent formate compounds. After 15 cycles, the hfac supply was depleted, resulting in no etching occurring between 12 and 15 cycles, and a reduction to the amount of carbon present on the surface. Instead, an increase in the thickness was observed, likely due to expansion of the film due to oxidation, since there was no etching step to reduce the film thickness. After the hfac was refilled, additional cycles resulted in continued etching, though at a lower rate. As was seen with ALE with formic acid, the etch rate was reduced as the number of cycles increased, corresponding to the enrichment of Co on the surface. With hfac, the effect is even more pronounced, with the Co content on the surface reaching 45% of the total amount of CoFeB.

Despite this, the higher overall etch rate even after multiple cycles indicates that the etching of Co and Fe is higher than it is for formic acid, even though the selectivity of Fe over Co may be higher. In contrast with previous results with formic acid, the amount of carbon on the surface was never higher than it was initially. Fluorine was detected on the surface as CF_x , indicating that some hfac remains on the surface, as was the case for formic acid, but the reduction in carbon content indicates that it is not as much of a problem as it was for the formic-acid-based process. The selectivity of CoFeB over W was found to be 6, though the etch rate of W was found to not be significantly different from zero, with a p -value of 0.358 indicating that the variance in SEM measurements was greater than the variations in thickness that were measured.

Overall, both formic-acid- and hfac-based cyclic processes demonstrated etching at a sub nm per cycle rate, though enrichment of Co was observed due to differences in selectivity between it and Fe, which may have been enhanced by the formation of the mixed valence Co_3O_4 after plasma oxidation.

Chapter 6. Summary

The etching of two important materials for novel devices, Ru and CoFeB, was investigated in this work. As the size of devices and interconnecting metal wires shrinks, these new materials become increasingly important as an avenue for improved performance, making an understanding of how they can be patterned critical to the success of next-generation technology. At the nanoscale, controllability of the etching process has become more important to the results, as the margin for error becomes smaller. Techniques such as atomic layer etching use multiple steps to improve the control of etching process through successive surface modification and etching steps that synergize with each other to provide selectivity. In this work, a thermochemical approach was used as the basis for investigating the effect of surface modification steps. The enhanced reactivity of ions and radicals present in plasma was used to overcome thermodynamic barriers to the formation of etch-enabling species. Kinetic modeling was used in combination with experimental diagnostics and characterization in order to understand the mechanisms that drove etching, allowing the selectivity and etch profile of the processes to be optimized.

For Ru to be integrated into the back-end-of-line, it must be subtractively patterned to form features with vertical profiles and low roughness while maintaining a high selectivity to the hard mask to prevent drift of the critical dimensions through mask growth or etching. While current O_2/Cl_2 RIE processes are able to deliver anisotropy, they do so at the cost of selectivity due to the addition of chlorine and application of high bias to drive ions to the surface at high energy. In this work, a novel Ru plasma etching process was developed. Using N_2 plasma, RuN can be formed on the surface the film. This layer acts to inhibit etching by O_2 plasma. The selectivity between Ru and RuN can be exploited to create an anisotropic process without energetic ions or corrosive

chemistry. Without ions, the RuN passivation layer withstood etching for multiple minutes. In combination with a H₂ plasma step that was used to remove RuN, a cyclic etching process was created. This N₂/H₂/O₂ process etched blanket film Ru samples at a rate of 3.6 nm per cycle when ions were present, but when ions were blocked, did not etch. Extending this process to patterned samples, where the ion flux to the sidewall is much lower than it is to the bottom of the trench resulted in vertical etch profiles. The N₂ plasma step was shown to be critical to the anisotropy of the process, with oxygen radicals etching laterally except when RuN was present to passivate the sidewalls. The H₂ plasma step was shown to be key to creating vertical sidewalls through the reduction of RuN at the bottom and corners of the trench, allowing the O₂ plasma step to etch vertically. The process demonstrated anisotropy as high as 18, and selectivity vs. the SiO₂ hard mask of 15 while resulting in lower surface roughness, resistivity, and aspect ratio dependence.

The etching of CoFeB in magnetic tunnel junction stacks is limited by redeposition during ion beam etching, making a chemical etch-based process necessary. Atomic layer etching is a good candidate for etching the thin magnetic CoFeB layers to avoid redeposition and harsh chemistry, such as chlorine, which degrades performance of the CoFeB. In this work, etching of CoFeB was explored using O₂ plasma to oxidize the surface, ensuring the metals were in +2/+3 oxidation states to react with organic vapor to form volatile etch products. Formic acid and hexafluoroacetylacetone (hfac) were used as the etchant in the vapor phase and were shown to etch CoFeB. In both cases, Co enrichment occurred likely due to the formation of mixed valence Co₃O₄ by plasma oxidation, inhibiting the formation of Co (II) etch products. While the etch rate of CoFeB was higher at 0.55 nm per cycle with hfac, compared to 0.26 nm per cycle with formic acid vapor, due to the increased volatility of hfac-based products, the enrichment of Co was also greater.

Appendices

Appendix A. Additional Data

Table A.1. Etching chemistry of Ru in literature. If multiple conditions are reported, the standard condition or condition with the highest etch rate is listed.

Material	Process	Ru/H.M. Selectivity	Etch Rate	Source
RuO ₂	O ₂ plasma	--	9 nm/min.	(Eung-Jik Lee et al., 1998)
Ru		15 vs TiN	22 nm/min.	(Hwang et al., 2016)
Ru		--	10 nm/min.	(Kim et al., 2002)
Ru		--	3 nm/min.	(Shamiryan et al., 2005)
Ru	Ar plasma	--	No etch	(Hsu et al., 2006)
Ru		4 vs TiN	78 nm/min.	(Hwang et al., 2016; Hwang et al., 2015)
Ru	O ₂ + Ar plasma	--	5 nm/min.	(Hsu et al., 2006)
Ru		4 vs TiN	32 nm/min.	(Hwang et al., 2016)
Ru	Cl ₂ plasma	--	5 nm/min.	(Kim et al., 2002)
Ru		--	No etch	(Shamiryan et al., 2005)
Ru	O ₂ + Cl ₂ plasma	6 vs SiO ₂	46 nm/min.	(Paolillo et al., 2018)
RuO ₂		--	46 nm/min.	(Eung-Jik Lee et al., 1998)
Ru		5 vs SiO ₂	56 nm/min.	(Kim et al., 2002)
Ru		--	42 nm/min.	(Shamiryan et al., 2005)
Ru		--	130 nm/min.	(Yunogami & Nojiri, 2000)

Ru		1.4 vs SiO ₂	22 nm/min.	(Kim et al., 2003)
Ru	O ₂ + Cl ₂ + Ar plasma	--	30 nm/min.	(Hsu et al., 2006)
RuO ₂	O ₂ + CF ₄ plasma	--	39 nm/min.	(Eung-Jik Lee et al., 1998)
Ru		--	5 nm/min.	(Shamiryan et al., 2005)
RuO ₂	O ₂ + N ₂ plasma	--	20 nm/min.	(Eung-Jik Lee et al., 1998)
Ru	O ₂ + CH ₄ + Ar plasma	4 vs TiN	25 nm/min.	(Hwang et al., 2016)
RuO ₂	O ₂ + C ₂ F ₄ H ₂ plasma	4 vs SiO ₂	160 nm/min.	(Pan & Desu, 1994)
Ru	Ar + CH ₄ plasma	3 vs TiN	43 nm/min.	(Hwang et al., 2016)
Ru	Ar + CH ₃ OH plasma	13 vs TiN	20 nm/min.	(Hwang et al., 2015)
Ru	O ₃ gas	--	950 nm/min.	(Nakahara et al., 2001)
Ru	VUV O ₂ /HCOOH ALE	--	0.12 nm/cycle	(Coffey et al., 2021)
Ru	Electrochemical ALE	--	0.12 nm/cycle	(Gong & Akolkar, 2020)
Ru	5.7% NaOCl solution	--	130 nm/min.	(Segaud et al., 2009)
Ru	2% NaOCl solution	--	3.5 nm/min.	(Le et al., 2023)
Ru	10 mM Ce ⁺⁴ solution	--	0.8 nm/min.	(Philipsen et al., 2019)
Ru	HIO ₄ + TMAH solution	--	8 nm/min.	(Le et al., 2023)
Ru	CF ₄ /Ar plasma ALE	--	1.2 nm/cycle	(Kim et al., 2023)
Ru	CHF ₃ /Ar plasma ALE	--	0.6 nm/cycle	(Kim et al., 2023)
Ru	C ₄ F ₈ /Ar plasma ALE	--	1.5 nm/cycle	(Kim et al., 2023)
Ru	O radical/Ar ion beam ALE	6 vs. SiO ₂	0.08 nm/cycle	(San Kim et al., 2024)

Ru	E-beam/O ₂ + Cl ₂ + Ar remote plasma	6 vs. Ta	0.6 nm/min.	(Li et al., 2025)
Ru	O radical/Acac vapor ALE	--	0.4 nm/cycle	(Lee, Kim, et al., 2025)
Ru	O ₂ + Ar plasma/Formic acid vapor ALE	Inf. Vs SiO ₂	0.21 nm/cycle	(Kang et al., 2026)

Table A.2. Thermodynamic properties of species involving in etching CoFeB. Data taken from (M.W. Chase et al., 1985; Outotec, 2023; Manuel A. V. Ribeiro Da Silva & M. Luisa C. C. H. Ferrão, 1988; Manuel A. V. Ribeiro da Silva & Maria Luísa C. C. H. Ferrão, 1988; Ribeiro da Silva et al., 1996)

Species	S° (J/mol-K)	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)
O _{2(g)}	205.15	0	0
H _{2(g)}	130.68	0	0
C _(s)	5.74	0	0
Fe _(s)	27.32	0	0
Co _(s)	30.04	0	0
B _(s)	5.83	0	0
CO _{2(g)}	213.80	-393.52	-394.39
H ₂ O _(l)	69.95	-285.83	-237.14
H ₂ O _(g)	188.83	-241.83	-228.58
HCOOH _(l)	129	-425	-361.4
HCOOH _(g)	247.1	-378.7	-350.5
C ₅ H ₈ O _{2(g)}	236.8	-423.8	-268.83
C ₅ H ₂ F ₆ O _{2(g)}	474.4	-1582	-1433.37
CoO _(s)	52.99	-237.74	-213.99
Co ₃ O _{4(s)}	114.29	-910.04	-794.87
Co(HCOO) _{2(a)}	41.84	-934.58	-773.38
Co(C ₅ H ₇ O ₂) _{2(s)}	340.5	-868	-548.39
Co(C ₅ H ₇ O ₂) _{2(g)}	650.6	-751	-523.84
Co(C ₅ H ₇ O ₂) _{3(s)}	496.3	-1234	-754.749
Co(C ₅ H ₇ O ₂) _{3(g)}	878.9	-1116	-750.821
Co(C ₅ HF ₆ O ₂) _{2(s)}	524.7	-4009	-3615.31
Co(C ₅ HF ₆ O ₂) _{2(g)}	807.4	-3909	-3599.59
Fe ₂ O _{3(s)}	87.4	-825.50	-743.52
Fe ₃ O _{4(s)}	145.27	-1120.89	-1017.44
Fe(HCOO) _{3(a)}	36.543	-1325.03	-1080.71
Fe(C ₅ H ₇ O ₂) _{3(s)}	486.9	-1315	-833.76
Fe(C ₅ H ₇ O ₂) _{3(g)}	798.8	-1186	-797.75
Fe(C ₅ HF ₆ O ₂) _{3(s)}	763.3	-5115	-4522.67
Fe(C ₅ HF ₆ O ₂) _{3(g)}	1102.9	-4995	-4503.92

Appendix B. Chemkin Plasma Modeling

Ansys Chemkin, a software package for modeling of chemical reaction systems, was used to model N₂ and O₂ plasmas in this work. A one-dimensional model involving electron, neutral, and ion collisions in the bulk plasma, as well as wall reactions, was used. Inputs provided include thermodynamic properties of the gas phase species as shown in Table A.3 and reaction rates as shown in Table A.4 in the modified Arrhenius format:

$$k = AT^B \exp(-E/T) \quad (\text{B. 1})$$

Where T is the temperature in eV of electrons, in the case of electron collisions, and ions or neutrals otherwise, and A , B , and E are constants determined by fitting the integral of the cross-section of the reaction with respect to electron energy times the electron energy distribution, which was assumed to be Maxwellian in this work.

Table A.3. List of species used in Chemkin modeling. Excited species are denoted with (*), and the electronic configuration and energy of species are listed relative to the ground state of the atom or molecule. The dissociation energy of the diatomic species is listed for the ground state atoms.

Species	Electronic Configuration	Energy above ground state (eV)
e^-	--	--
O	^3P	(5.12, Dissociation)
O^+	$^4S^o$	13.61
O^-	$^2P^o$	1.46
O^*	^1D	1.97
O_2	$X\ ^3\Sigma_g^-$	0
O_2^+	$X\ ^2\Pi_g$	12.14
O_2^*	$a\ ^1\Delta_g$	0.98
N	$^4S^o$	(9.76, Dissociation)
N^+	^3P	14.54
N^*	$^2D^o$	2.38
N^{**}	$^2P^o$	3.57
N_2	$X\ ^1\Sigma_g^+$	0
N_2^+	$X\ ^2\Sigma_g^+$	15.58
N_2^*	$A\ ^3\Sigma_u^+$	6.17

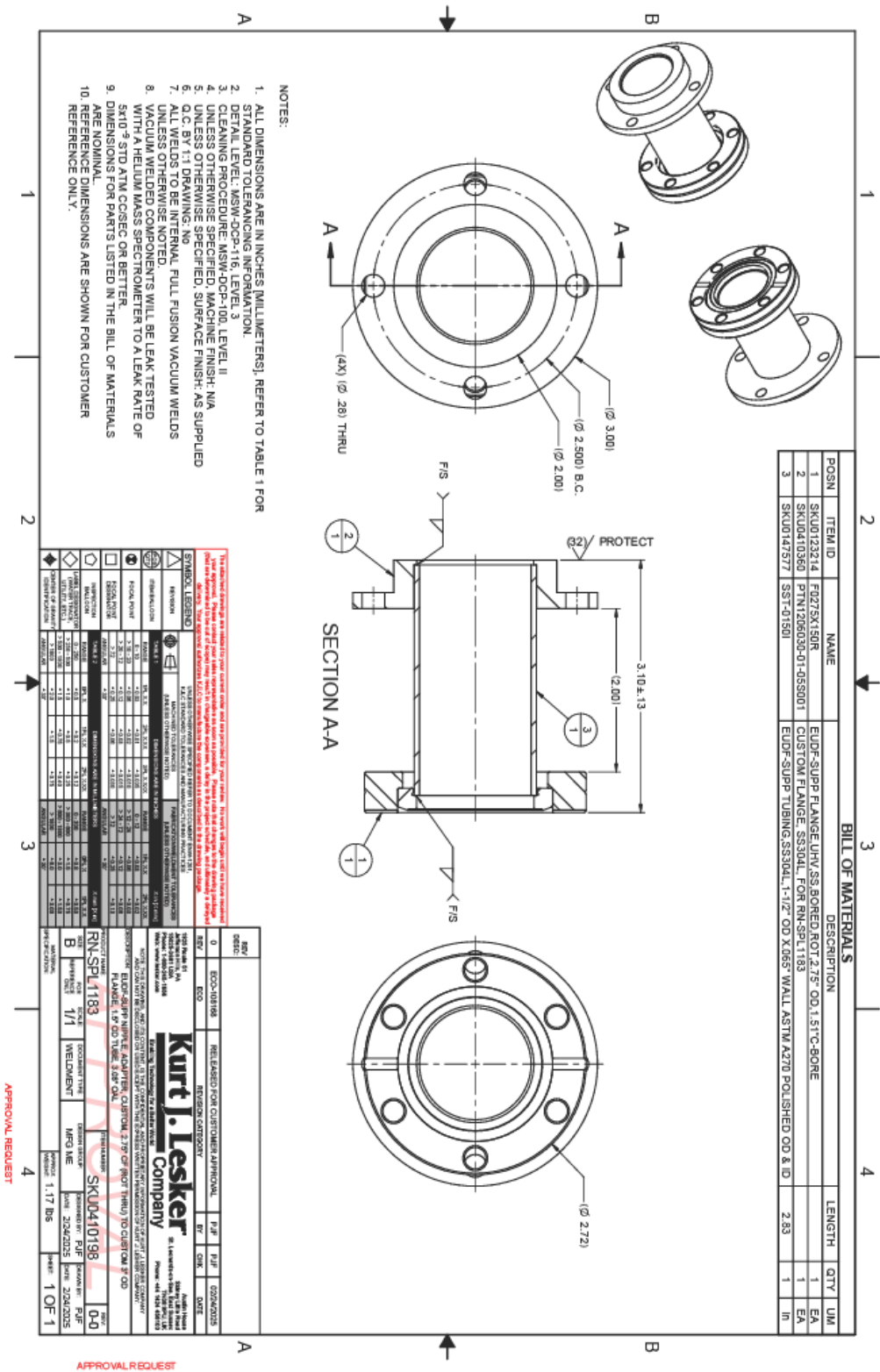
Table A.4. Reactions in the O₂ plasma model. Reaction rates are taken from (Lieberman & Lichtenberg, 2005)

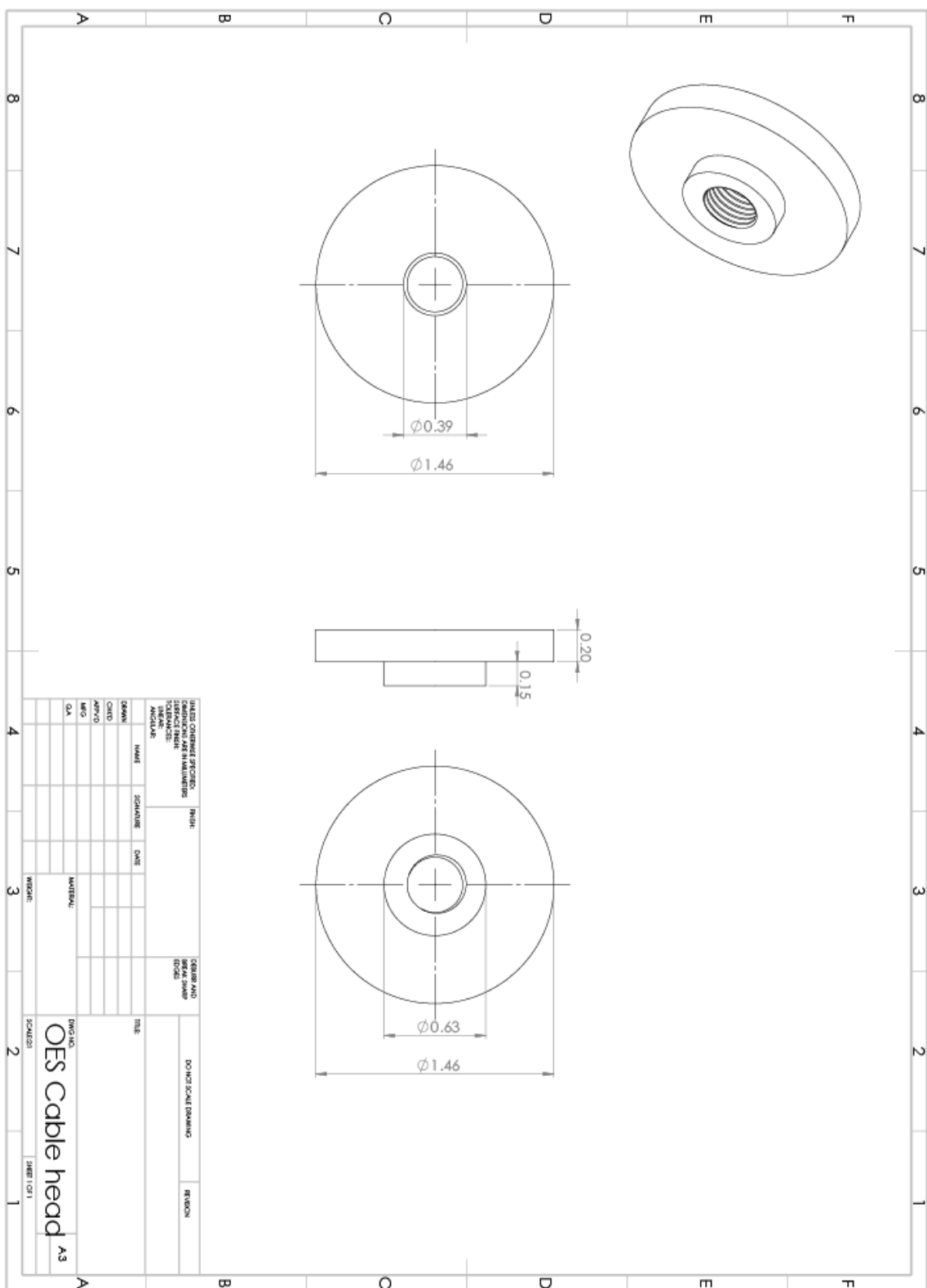
Reaction	A (cm ³ /s)	B	E (eV)
$e^- + O_2 \rightarrow O^- + O$	1.07E-09	-1.391	6.26
$e^- + O_2 \rightarrow 2O + e^-$	6.86E-09	0	6.29
$e^- + O_2 \rightarrow O_2^+ + 2e^-$	2.34E-09	1.03	12.29
$e^- + O^- \rightarrow O + 2e^-$	5.47E-08	0.324	2.98
$e^- + O_2^+ \rightarrow 2O$	2.20E-08	-0.5	0
$O^- + O_2^+ \rightarrow O + O_2$	2.60E-08	0	0
$O^- + O \rightarrow O_2 + e^-$	3.00E-10	0	0
$O^- + O_2^+ \rightarrow 3O$	2.60E-08	0	0
$e^- + O_2 \rightarrow O^- + O^+ + e^-$	7.10E-11	0.5	17
$e^- + O_2 \rightarrow O + O^+ + 2e^-$	1.88E-10	1.669	16.81
$e^- + O \rightarrow O^+ + 2e^-$	9.00E-09	0.7	13.6
$O^- + O^+ \rightarrow 2O$	4.00E-08	0	0
$O^+ + O_2 \rightarrow O + O_2^+$	2.00E-11	0	0
$e^- + O_2 \rightarrow O_2^* + e^-$	1.37E-09	0	2.14
$e^- + O_2^* \rightarrow O_2 + e^-$	2.06E-09	0	1.163
$e^- + O_2^* \rightarrow O + O^-$	4.19E-09	-1.376	5.19
$O_2^* + O_2 \rightarrow 2O_2$	2.20E-18	0	0
$O_2^* + O \rightarrow O_2 + O$	7.00E-16	0	0
$e^- + O_2 \rightarrow O + O^* + e^-$	3.49E-08	0	5.92
$e^- + O \rightarrow O^* + e^-$	4.54E-09	0	2.36
$e^- + O^* \rightarrow O + e^-$	8.17E-09	0	0.4
$e^- + O^* \rightarrow O^+ + 2e^-$	9.00E-09	0.7	11.6
$O^* + O \rightarrow 2O$	8.00E-12	0	0
$O^* + O_2 \rightarrow O + O_2$	4.10E-11	0	0
$O^* + O_2 \rightarrow O + O_2^*$	1.00E-12	0	0
$O_2^+ + e^- \rightarrow O_2$ (wall)	1	0	0
$O^+ + e^- \rightarrow O$ (wall)	1	0	0
$O_2^* \rightarrow O_2$ (wall)	1	0	0
$O^* \rightarrow O$ (wall)	1	0	0
$O \rightarrow 0.5O_2$ (wall)	0.007	0	0
$O^* \rightarrow 0.5O_2$ (wall)	0.007	0	0

Table A.5. Reactions in the N₂ plasma model. Reaction rates and collision cross-sections are taken from (*IAA database*; Kawaguchi et al., 2021; Kim & Desclaux, 2002; Kossyi et al., 1992; Song et al., 2023; Thorsteinsson & Gudmundsson, 2009; Wu et al., 2024)

Reaction	A (cm ³ /s)	B	E (eV)
$e^- + \text{N}_2 \rightarrow \text{N}_2^* + e^-$	1.19E-08	-0.44	6.86
$e^- + \text{N}_2 \rightarrow \text{N}_2^+ + 2e^-$	1.04E-08	0.63	16.52
$e^- + \text{N}_2 \rightarrow 2\text{N} + e^-$	1.68E-09	-1.49	10.37
$e^- + \text{N}_2 \rightarrow \text{N} + \text{N}^* + e^-$	1.64E-08	0.32	15.65
$e^- + \text{N}_2 \rightarrow \text{N} + \text{N}^+ + 2e^-$	1.68E-09	0.88	27.02
$e^- + \text{N}_2^* \rightarrow \text{N}_2^+ + 2e^-$	1.79E-08	0.66	11.06
$e^- + \text{N}_2^+ \rightarrow 2\text{N}^*$	1.03E-08	-1.46	0.33
$e^- + \text{N}_2^+ \rightarrow \text{N} + \text{N}^*$	8.26E-09	-1.46	0.33
$e^- + \text{N}_2^+ \rightarrow \text{N} + \text{N}^{**}$	2.07E-09	-1.46	0.33
$e^- + \text{N}_2^+ \rightarrow \text{N} + \text{N}^+ + e^-$	1.45E-08	0.19	8.97
$e^- + \text{N}_2^+ \rightarrow 2\text{N}^+ + 2e^-$	6.54E-10	0.95	29.36
$e^- + \text{N} \rightarrow \text{N}^* + e^-$	4.00E-08	-0.51	4.92
$e^- + \text{N} \rightarrow \text{N}^{**} + e^-$	1.44E-08	-0.61	5.32
$e^- + \text{N} \rightarrow \text{N}^+ + 2e^-$	4.39E-09	0.79	14.42
$e^- + \text{N}^* \rightarrow \text{N}^{**} + e^-$	1.04E-08	-0.18	1.60
$e^- + \text{N}^* \rightarrow \text{N}^+ + 2e^-$	1.56E-08	0.53	13.02
$e^- + \text{N}^{**} \rightarrow \text{N}^+ + 2e^-$	1.52E-08	0.53	13.04
$\text{N}^* + \text{N}^{**} \rightarrow \text{N}_2^+ + e^-$	1.00E-12	0	0
$\text{N} + \text{N}^* \rightarrow 2\text{N}$	1.36E-14	0.23	2.69E-3
$\text{N} + \text{N}^{**} \rightarrow 2\text{N}$	6.20E-13	0	0
$\text{N} + \text{N}^{**} \rightarrow \text{N} + \text{N}^*$	1.80E-12	0	0
$\text{N} + \text{N}_2^* \rightarrow \text{N}^{**} + \text{N}_2$	5.00E-11	0	0
$\text{N}^* + \text{N}_2 \rightarrow \text{N} + \text{N}_2$	1.30E-14	0	0
$\text{N}^{**} + \text{N}_2 \rightarrow \text{N} + \text{N}_2$	3.30E-17	0	0
$\text{N}^{**} + \text{N}_2 \rightarrow \text{N}^* + \text{N}_2$	2.00E-18	0	0
$\text{N}_2 + \text{N}_2^* \rightarrow 2\text{N}_2$	3.00E-18	0	0
$\text{N} + \text{N}_2^+ \rightarrow \text{N}^+ + \text{N}_2$	2.40E-15	1	0

Appendix C. Custom Part Drawings





Appendix D. Plasmatherm 770 ICP Standard Operating Procedure

Introduction: The newer SLR 770 is used to etch Al, Pt and III-V semiconductors using either methane, Cl₂ or HBR chemistries. An inductively coupled plasma (ICP) generates a very dense plasma near the top of the electrode. A 2nd RIE generator which is capacitively coupled to the wafer chuck is used to independently bias the substrate. In this way, high selectivities and high etch rates can be obtained. Also it can use as RIE etch, just turn ICP power to zero.

All samples must be mounted to a 4 inch SiO₂ wafer. Through-wafer etching also requires a 4 inch SiO₂ carrier wafer since backside He cooling is used. After long runs or many short runs the chamber may get dirty as evidenced by a poor base pressure ($>8.0 \text{ E-6}$). Do not proceed if the base pressure is too high or the leak-back rate is too high ($>.3 \text{ mT}$ in 1 minute).

Additionally a clean must be run (recipe O₂clean for 30 minutes) every time when your process has been finished. Any recipe changes must be developed and or verified by nanostaff before entering it into the recipe data bank.

Safety Check list:

1. Previous entry in logbook shows no problem.
2. Check the exhaust gauge(magnehelic gauge) at top of sink on the left side of the machine. If it is below 2.5 inch, please do not run the machine and report to nanostaff. See the picture I.

System Operation:

1. Place system in Standby Mode (if it isn't already) by clicking on Standby button. Move the mouse if the screen is blanked by the screen saver.

2. Verify from chamber view that chamber pressure is $<.5$ mT and chamber is being pumped (Turbo and Mech Pump are green in the drawing). Verify that the utilities: air, water, power are in the green zone also (bottom right of screen).

3. Check Log book for any problems previous user may have had. Alternately you can check any recent alarms by going to

Display -> Alarm History.

Do not proceed if there are unresolved problems.

4. Vent the loadlock:

Utilities -> Loadlock -> Vent

Set view to OVERVIEW so that both chambers' status can be monitored. The loadlock (leftmost chamber) will first turn red and then read ATMOSPHERE on the drawing when it is vented which takes 3 or 4 minutes.

NOTE: Make any thickness or depth measurements before loading if you need to measure selectivity eg photoresist or oxide thickness on Nanospec or Alphastep or Dektak8.

CAUTION: Your wafer should be cleaned and hard baked if it has photoresist. Wafers or pieces smaller than 4 inch must be glued to a 4 inch carrier wafer using very small drops of photoresist or other approved material. For very thick resists, (>10 microns) you must remove the edge bead otherwise the wafer will stick to the clamp at the end of the etch and will break.

CAUTION: Wear a face mask whenever loading and unloading a wafer.

5. Lift the hinged loadlock cover and load your wafer with flat facing in and side to be etched facing up. It must sit snug against the loading arm pocket.

6. Close and hold the cover and begin pump down by selecting:

Utilities -> Loadlock -> Pump

7. When the loadlock pressure is $<.3$ Torr, transfer the wafer to the process chamber by selecting:

Service -> Maintenance -> Wafer Handling

Press Load at the bottom left of the dialog screen. An animation shows wafer being transferred. When wafer transfer is complete (you can look thru the viewport with the desk lamp to the right of the machine), press EXIT button to exit screen.

8. Wait 3-4 minutes and then run a Leak-check:

Make sure ion gauge is off

Utilities -> Ion Gauge Off

Service -> Maintenance -> Leak Test

Push Start in Dialog box

NOTE: System pumps chamber down to base pressure, closes gate valve and after a minute begins displaying instantaneous leak rate. Note the starting chamber pressure, and then the pressure after 1 minute (Top box). Leakback pressure must be $<.3$ mTorr per minute. Press End in Dialog box to end test. In chamber view, make sure the throttle valve is open and chamber pressure is $<.3$ mT.

9. The first step of every recipe is a pump-down step which is set at $8 \text{ E-}6$. If the chamber is dirty or hot (after several runs), the chamber may take a long time to complete the step. Also if

the ion gauge is contaminated it may need degassing. To degas the ion gauge it must be off first (as in previous step). To Degas:

Service -> Maintenance -> Degas

Push the start button and allow a 2 minute degas (burn off). Then push Stop to end the degas.

10. Edit recipe:

Use most recent data from logsheet or test run for etch rate data. Divide desired thickness (μm) by etch rate to get time (min).

CAUTION: Etch rate is a function of chamber history, % exposed III-V or Metal and many other factors. When in doubt make a test run with an identical sample. Do not change flow, pressure or power without consulting with Nanostaff.

Process -> Chamber -> Open

Select recipe from list and press OK. Check each step against the step in the log book for time, power, gas flows etc. If a change needs to be made report it to lab management. Double click on Etch Step to set the etch time. Input the etch time in the time box at the bottom left of the screen. Make sure correct loop start step is highlighted in the Dialog Box (as this determines the loop starting point).

Click OK

Save Recipe? -> Yes

Exit

11. Load and run recipe

Process -> Chamber -> Load

Select recipe to load, Press “OK”. Verify desired recipe is shown in “Process” box at lower right screen. Put machine into Ready mode, press Ready button. Press Run to begin processing

12. Verify in Dialog box that correct recipe is running and parameters are correct. It is a good idea, if at all possible, to stay and make sure the process runs correctly. The first step is always a pump down step and is usually set to $8\text{E-}6$. If the system is taking longer than 10 minutes to complete this step AND the base pressure is $<1\text{E-}5$, press END STEP at the bottom of the screen to advance to the next step. This may be necessary if many runs or a long run has just been completed (ie chamber is hot).

13. After etch is completed, click OK in Dialog box, if the Dialog box is present (Depends on how program was run.)

14. Put machine in Standby mode by pressing Standby button.

15. Transfer wafer to loadlock:

Service -> Maintenance -> Wafer Handling

Press Unload at bottom of screen

After wafer is in Loadlock press Exit

16. Vent Loadlock as before:

Go to OVERVIEW View then,

Utilities -> Loadlock -> Vent

17. After lock vents, remove wafer close lid and pump loadlock down again:

Utilities -> Loadlock -> Pump

18. Leave system in Standby mode and record all data in logbook.

Miscellaneous Problems:

SYSTEM LOCKUP

Occasionally the system may lock up and not respond to any commands. Try exiting the Program Sysmon if possible or if that doesn't work try exiting windows and restarting (type win after getting the DOS prompt). If this fails, open the lower panel and press the red reset button on the computer at the bottom. This should reboot all the software and a dialog box requesting user and password will come up. Enter 3333 in both boxes. If a wafer is in the process chamber it should still know this. If not get help.

IDENTIFYING & ACKNOWLEDGING ALARMS

If something went wrong and you are not sure what happened (check info box at the bottom of screen first) go to:

Display -> Alarm History

Date and time appear next to each alarm and can help you identify what went wrong. Press ALARM SILENCE at the bottom right of screen to silence an alarm or at the end of a run. If there is a problem, the HOLD button illuminates when the alarm is silenced. Push the HOLD button to put the system back in Standby or Ready. If the alarm condition is still present, however, the alarm will continue to go off. In this case the problem must be fixed first.

UNLOADING PROBLEMS

Wafer transfer problems generally occur because of either poor procedure of attaching a wafer to a carrier or thick PR at the wafer edge which gets sticky with heat causing the wafer to stick to the clamp and break in the process chamber. For thicker resist, use edge bead removal or keep your etches short. For gluing wafers use very small dabs of photoresist or approved material and bake thoroughly. If a wafer breaks or gets stuck in process chamber, you must get help. Do not attempt to fix the problem yourself.

CHAMBER CLEANING

As mentioned previously, an oxygen plasma clean (recipe O2Clean) should be run every time when etch substrate material been changed. Load the dummy clean wafer kept at the machine and load the recipe following standard procedures. After clean run please follow up one 5 min dummy run. Use the recipe you are going to etch for dummy run. And use the dummy wafer coated by photoresist. Make the entry in the log book that the O2Clean and dummy were run. There is no charge for this.

ADDITIONAL RECIPES

An approved recipe list is kept at the machine. You must get approval and help in writing your own recipe since small changes in a parameter can have a large detrimental effect on the process and machine. Once the recipe is approved it will be added to the recipe list. Anyone may run any of the posted recipes but may change only the etch time, nothing else.

SYSTEM ABORT

The abort button at the bottom of the screen aborts the entire recipe but may cause a system crash. If possible try using End Step several times first.

EMERGENCY SHUT OFF

The big red button at the front side of the machine will kill all the power and is to be used only in extreme emergency ie smoke or burning smell coming from the machine, etc. Do NOT attempt to turn on the machine if it is shut down in this manner.

GAS SUSPECTED IN CHAMBER

This alarm may occur from a system abort, a logic error or a real problem. If the turbo-pump is still on (green) and the throttle valve is closed (as seen in Chamber View) try pumping the system in the Standby mode by selecting:

Service -> Maintenance -> Pump -> System

Procedure for gluing silicon wafers together:

Small pieces wafer (< 4 inch) must be glued to a 4 inch SiO₂ carrier wafer in order for the loading mechanism to work. Additionally, if a wafer is to be etched all the way through, the wafer must either have an oxide on the backside or be glued to a 2nd SiO₂ 4 inch wafer. This is because backside Helium cooling is used on the wafer chuck and once the etch breaks through, the helium leaks into the chamber, raises the pressure and shuts down the machine.

The SiO₂ carrier wafer must be very clean like the sample to be etched. The wafer has to be thermally oxidized silicon with 5000Å thickness. A bare silicon carrier wafer will contaminate your III-V etch process due to etch.

The following procedure must be used for etching either wafer pieces or all the way through the wafer. It is extremely important that no air bubbles be trapped in the PR as this will cause the

piece to flip over during pumpdown or etch. You should firmly rub the piece onto the 4 inch wafer to remove air and/or use the vacuum bake oven. Additionally grooves on the underside of your piece will aid in allowing air to escape.

PIECES

1. Use an eyedropper or Q-tip to deposit a small drop of AZ5214 resist (or equivalent) on the backside of your piece.

2. Then carefully center the backside of your piece onto the front-side of the carrier wafer and press down firmly. Do NOT use too much resist as this will be squeezed out from the back when you press down and can cause problems.

3. Bake your sample on a hot plate at 120°C for at least 3 minutes. This hardens the resist. Do not allow the backside of the carrier wafer to become contaminated (eg from the hot plate).

4. Let your sample cool and bring it to the Cl2 Etch machine and follow the loading procedures as outlined in the SLR 770 ICP spec.

WHOLE WAFERS

1. Use an eyedropper as above but put 2 or 3 small drops on the backside of your 4 inch SiO₂ wafer near the center spaced about 1/2 inch apart.

2. Carefully center the backside of your wafer over the carrier wafer and press down firmly. Make sure the flats for both wafers line up before pressing the substrates together.

3. Bake your sample on a hot plate at 120°C for at least 3 minutes. This hardens the resist. Do not allow the backside of the carrier wafer to become contaminated (eg from the hot plate).

4. Let your sample cool and bring it to the III-V machine and follow the loading procedures as outlined in the SLR 770 ICP spec.

Additional Information on III-V RIE

1. For resist thicknesses $< 2\text{-}3\text{ }\mu\text{m}$, edge bead removal is probably not necessary if the resist is baked. Thicker films $> 8\mu\text{m}$, can outgas and cause clamping problems. Removal of the edge bead is advised in these cases.

2. Resist profile will affect the etch and sidewall profile. When baking resist, avoid too high a temperature such that the resist flows (unless you are trying to get a taper).

1. Small pieces wafer can be “glued” to a 4 inch SiO_2 silicon wafer using a dab of PR. A bare silicon wafer will etch down and contaminate the etch chamber. In any event, you must use a 4 inch SiO_2 wafer as a carrier.

3. III-V etch rate is a function of exposed area (usually expressed as % open III-V). Etching slows down dramatically as the amount of exposed area goes up, so keeping track of exposed area is important. But Metal etch rate is not usually expressed as % open exposed area, because most time Metal etch time is very short.

4. A cleaning run is not normally needed unless the process chamber is opened and the etch substrate material is changed. If so the recipe is:

* 80sccm O_2 + 10 sccm Ar @12 mT

800W ICP + 100W RIE

* Make sure a blank wafer is on cathode to protect it

Appendix E. Vapor Chamber Standard Operating Procedure

CHEMICALS USED:

1. Formic Acid (HCOOH)
2. Hexafluoroacetylacetone (Hfac, $\text{C}_5\text{H}_2\text{F}_6\text{O}_2$)
3. Nitrogen (N_2)
4. Ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$)

EMERGENCY SHUTDOWN:

1. Turn off heaters for vaporizer, gas delivery line, and chamber.
2. Press Close on LFC and MFC controllers.
3. Close V1, V7, and V16 if open.
4. Open AV to remove gas from chamber.
5. Unplug vaporizer heater, LFC controller, and MFC controller.
6. Turn off cold trap power on the right side of the cold trap, as circled in Figure 2.

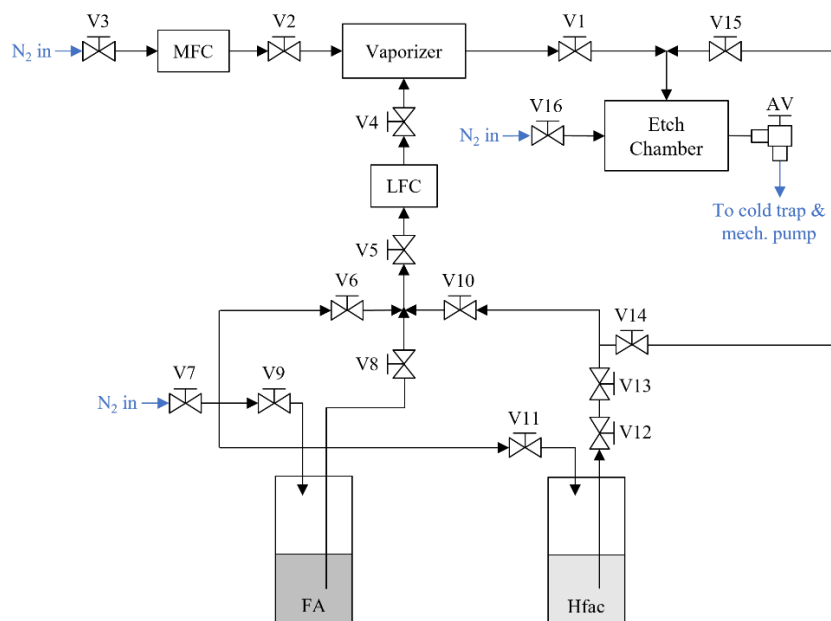


Figure 1. Vapor chamber schematic

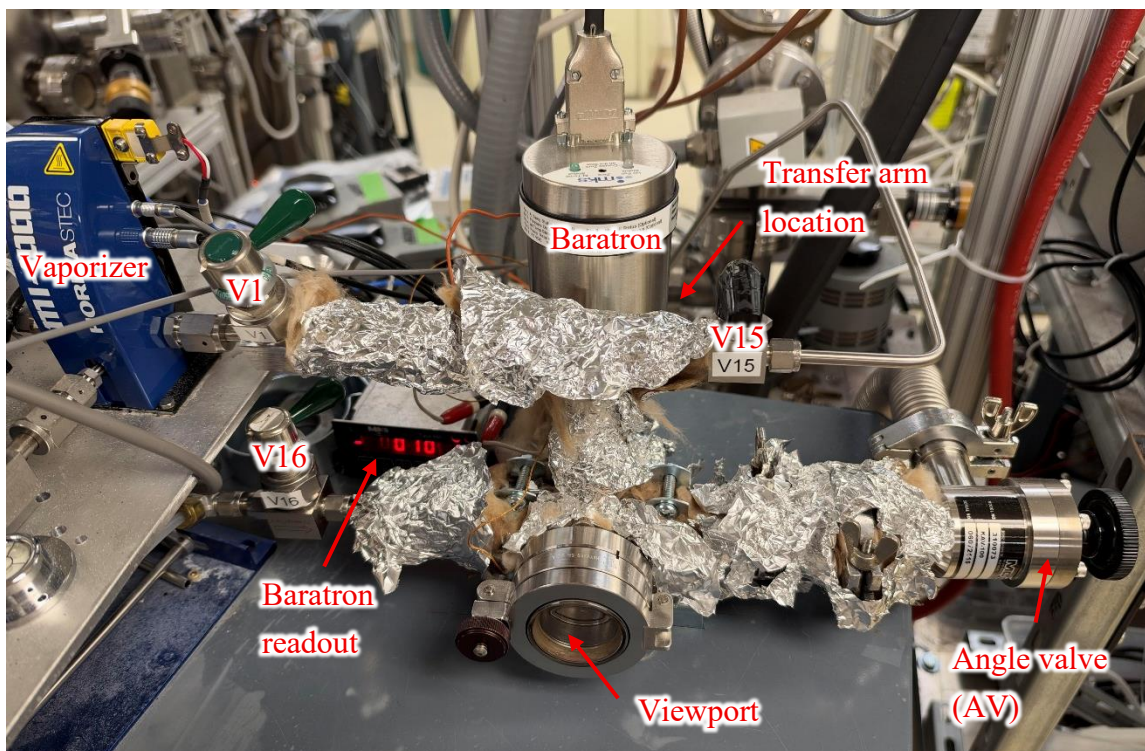


Figure 2. Photo of vapor chamber centered around the etch chamber itself.

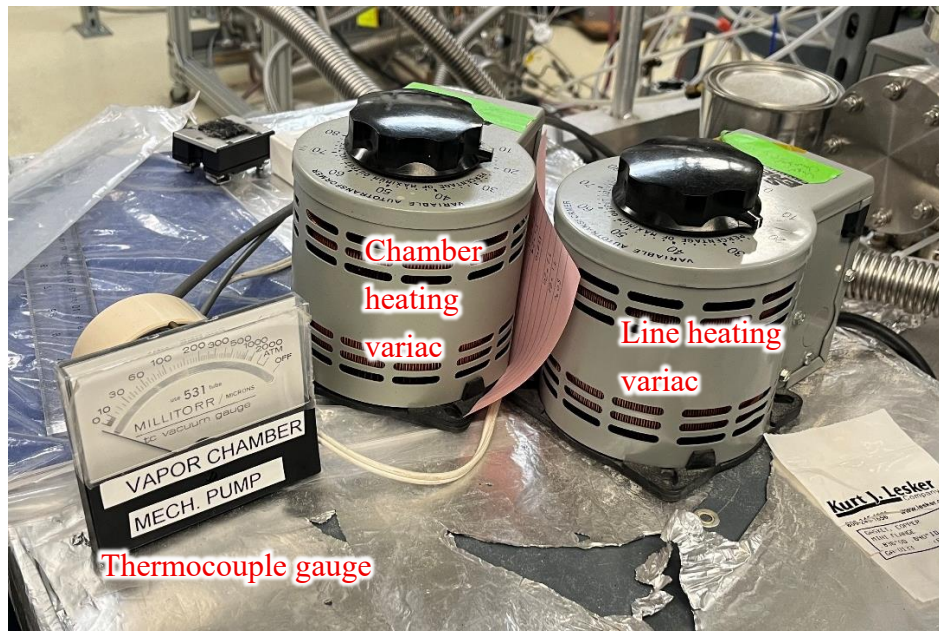


Figure 3. Photo of table behind vapor chamber with variacs and thermocouple gauge readout.



Figure 6. Coldwell after disassembling

STANDARD OPERATING PROCEDURE:

Steps 1-4 and 7-8 should be performed in order every time the process is run. Run step 5 for formic acid exposure, or step 6 for hexafluoroacetylacetone (hfac) exposure.

1. *Initial Check:* Make sure valves V1-V16 are closed, heaters are off, chamber is pumped down
 - a. Heaters should be off, vaporizer heater and thermocouples should show room temperature.
 - b. Cold trap should be on with all front panel LED lights lit up.
 - c. Angle valve to mechanical pump (AV) should be open, baratron gauge readout should show ~0.000 decaTorr (1 decaTorr = 10 Torr). Thermocouple gauge should read <10 mTorr.
 - d. Check the experimental log. If any issues were reported by the previous user, ensure that they have been resolved prior to operation. If the organic acid to be used has been run 15 times without refill, follow step 10 (formic acid) or 11 (hfac) to refill the ampoule.
2. *Prepare for Operation:*
 - a. Open the V1 to V5 in the numerical order, the order of opening is designed so that any formic acid from leaky LFC and/or valves would be carried away by N₂.
 - b. Turn on heaters. Allow approximately 30-60 minutes for the chamber to reach desired temperature, check with thermocouple.
 - i. For 80°C operation, set vaporizer heater to 80°C, line and chamber variacs to 21% output voltage.
 - ii. For 120°C operation, set vaporizer heater to 120°C, line and chamber variacs to 28% output voltage.
3. *Load Sample into Chamber:*
 - a. Close the injection valve to chamber (V1), and confirm that V15 is closed.
 - b. Close the valve to the mechanical pump (AV).
 - c. Open vent line valve (V16) slowly until viewport door opens. Pressure gauge should read approx. 76 decaTorr. Once the viewport door is open, close the vent line valve to minimize use of N₂.
 - d. Loosen transfer arm lock and bring arm forward by turning the rack and pinion handle until the stage is out of the vapor chamber.
 - e. Attach sample to stage using copper tape.
 - f. Retract transfer arm into the chamber by turning the rack and pinion handle. Check that the sample will not collide with the vapor delivery line. Position of the linear motion feedthrough should be set at 40 for the sample stage to be beneath vapor delivery line.

The feedthrough should be set to 80 if you do not want sample to be directly exposed to organic acid flow. Tighten the transfer arm lock.

4. *Pump Down Chamber:*

- a. Close viewport door and lock it.
- b. Close vent line valve (V16) after sample loading to minimize moisture adsorption.
- c. Open angle valve (AV) to mechanical pump slowly.
- d. Wait for pressure gauge to reach 0.000 decaTorr.

5. *Deliver Vapor to System (Formic Acid):*

- a. If hfac was previously used, perform step 9 first.
- b. Check that vent line valve (V16), bypass line valve (V6), and hfac valves (V10-V13) are closed.
- c. Ensure that valves V1-V5, and V8 are open.
- d. If the ampoule has not been repressurized (such as after replacing the liquid), follow step 12.
- e. To avoid accidental release of the viewport door if the chamber is overpressurized, ensure the door is closed with the screw handle (do not overtighten to avoid damaging the rubber gasket).
- f. Close valve (AV) to the mechanical pump.
- g. Press Cont on the N₂ MFC and Open on the organic acid LFC simultaneously. If simultaneous pressing is difficult to achieve, open N₂ first to minimize acid exposure.
- h. Allow the chamber to fill to the desired pressure (15-45 decaTorr), then press Close on both MFC & LFC. To accurately reach the desired pressure, press Close when the pressure is approximately 2 decaTorr below the target. Allow the sample to remain in the chamber for the desired etch time. Condensation should occur on the viewport door.
- i. Report the process conditions in the experimental logbook.
- j. Once process is finished, open the valve to the mechanical pump (AV) then press Open on the N₂ MFC to push out remaining formic acid in the vapor delivery line (this should take ~30 seconds). Press Off to stop N₂ MFC flow.
- k. Cycle purge the chamber (see step 7).

6. *Deliver Vapor to System (Hexafluoroacetylacetone):*

- a. If formic acid was previously used, perform step 9 first.
- b. Check that vent line valve (V16), bypass line valve (V6), and formic acid valve (V8) are closed.
- c. Ensure that valves V1-V5, and V10-V13 are open, but valves V14 and V15 are closed.
- d. If the ampoule has not been repressurized (such as after replacing the liquid), follow step 12.
- e. To avoid accidental release of the viewport door if the chamber is overpressurized, ensure the door is closed with the screw handle (do not overtighten to avoid damaging the rubber gasket).
- f. Close valve (AV) to the mechanical pump.
- g. Press Cont on the N₂ MFC and Open on the organic acid LFC simultaneously. If simultaneous pressing is difficult to achieve, open N₂ first to minimize acid exposure.
- h. Allow the chamber to fill to the desired pressure (15-45 decaTorr), then press Close on both MFC & LFC. To accurately reach the desired pressure, press Close when the pressure is approximately 2 decaTorr below the target. Allow the sample to remain in the chamber for the desired etch time. Condensation should occur on the viewport door.

- i. Report the process conditions in the experimental logbook.
 - j. Once process is finished, open the valve to the mechanical pump (AV) then press Open on the N₂ MFC to push out remaining formic acid in the vapor delivery line (this should take ~30 seconds). Press Off to stop N₂ MFC flow.
 - k. Cycle purge the chamber (see step 7).
7. *Cycle Purge the Vapor Chamber:*
- a. Ensure valves V1-V3 are open.
 - b. Close AV, then press Cont. on the N₂ MFC.
 - c. When pressure in the chamber reaches 10 decaTorr, press Close on the MFC.
 - d. Open AV to pump down the chamber
 - e. Repeat steps a-d two additional times.
8. *Unload Sample from Vapor Chamber:*
- a. The vapor chamber must have been cycle purged (see step 7) prior to opening it to atmosphere to ensure all organic vapors have been removed.
 - b. Close the valves to the chamber (V1 and V15).
 - c. Close the valve to the mechanical pump (AV).
 - d. Open vent line valve (V16) slowly until viewport door opens. Pressure gauge should read approx. 76 decaTorr.
 - e. Loosen transfer arm lock and bring arm forward by turning the rack and pinion handle until the stage is out of the vapor chamber.
 - f. Remove sample from stage. If another sample needs to be processed, attach it to the stage now using copper tape.
 - g. Retract transfer arm into the chamber by turning the rack and pinion handle. Check that the sample will not collide with the vapor delivery line. Position for stage to be beneath vapor delivery line is 30.

ADDITIONAL OPERATING PROCEDURE:

These additional steps do not need to be run every times, but may be needed when directed by the SOP above, or for the regular refilling of ampoules.

9. *Purge Organic Acid Delivery Lines:*
- a. Check that vent line valve (V16), bypass line valve (V6), formic acid valve (V8), hfac valve (V10-V13), and all FV valves are closed.
 - b. Ensure that valves V1-V5 are open.
 - c. With AV still open, press Cont. on the N₂ MFC and Open on the organic acid LFC simultaneously to let any remaining organic acid flow out for about 1 minute.
 - d. Open V7, then V6 to let N₂ from the bypass line push out any acid remaining in the 4 way junction.
 - e. Close V6, then V7. Press Close on both MFC and LFC.
 - f. To confirm that no liquid remains in the LFC lines, close AV, then press Cont. on the N₂ MFC and Open on the organic acid LFC simultaneously.
 - g. Press Close on both MFC and LFC when the pressure reaches 10 decaTorr.

- h. After determining if any condensation has appeared on the viewport, open AV to pump the chamber. If any condensation did appear, there is liquid remaining in the system, and the purging process should be repeated.
- i. To purge the hfac delivery line, start by closing V1 and V5.
- j. Open V13 and V14. Slowly open V15, ensuring that the pressure does not increase too quickly when the hfac bypass line is opened to the chamber.
- k. Allow the pump to remove hfac from the line. To check if there is still liquid remaining in the line, check if the pressures reported by the baratron and thermocouple gauges are higher than usual, and close AV temporarily to check the pressure rate-of-rise.
- l. Once the line has been pumped, close V14 and V15.

10. *Refill Ampoule (Formic Acid):*

- a. For sample exposure at 350 Torr of mixture pressure (MFC & LFC fully opened), ampoule can sustain approximately 15 exposure before needing a refill.
- b. Prior to removal of an ampoule, purge the liquid feed lines (see step 9).
- c. Check that all valves from V5-V15 are closed.
- d. For the formic acid ampoule, disconnect the Swagelok fitting between V9 and the T junction, then disconnect the VCR fitting between V8 and the 4-way junction.
- e. Remove the zip ties attaching the assembly to the leg of the table while holding the assembly to ensure it does not slip.
- f. Take the formic acid ampoule to the fume hood.
- g. Open valve V9 first, then valve V8 to relieve any pressure.
- h. Disconnect the CF connection between the 1.33" CF liquid feedthrough and the 1.33" to 2.75" CF zero-length adapter. Refill the ampoule, leaving about ½ inch below the steel-quartz joint for the doser tubing. Residue formic acid might present in the liquid delivery line due to the setup, use cleanroom wipes to wipe off the residual, safely dispose the wipes.
- i. Once ampoule is full, reconnect the 1.33" CF connection between the ampoule and the liquid feedthrough, then close both valves.
- j. Mount the assembly back on the leg of the table, using zip ties to secure it.
- k. Reconnect V8 and V9 to the vapor chamber lines. V8 requires a stainless steel VCR gasket (do not use an Ag-plated gasket as it may corrode).
- l. Pressurize the ampoule with V9 (see step 12).

11. *Refill Ampoule (Hexfluoroacetylacetone):*

- a. For sample exposure at 350 Torr of mixture pressure (MFC & LFC fully opened), ampoule can sustain approximately 15 exposure before needing a refill.
- b. Prior to removal of an ampoule, purge the liquid feed lines (see step 9). It is particularly important to ensure the hfac delivery line has been pumped to avoid accidental release.
- c. Wear PPE (gloves, goggles, and lab coat) to avoid exposure in the case of accidental release of hfac. Do not open the ampoule while others are working in the dry lab, and inform the other members of the lab prior to removal.
- d. Check that all valves from V5-V15 are closed.

- e. For the hfac ampoule, disconnect the Swagelok fitting between V11 and the flexible tubing. Since the tubing connected to the ampoule is long, be careful to not damage it while removing the ampoule.
- f. While holding a cleanroom wipe to the fixture, disconnect the VCR fitting between V12 and V13. If residual hfac was present in this small section of tubing, exit the area to avoid inhalation. After 30 minutes, the spill should have evaporated if caught by the cleanroom wipe.
- g. Remove the zip ties attaching the assembly to the leg of the table while holding the assembly to ensure it does not slip.
- h. Transfer the ampoule to the fume hood in room 1011.
- i. Open valve V11 first, then valve V12 to relieve any pressure.
- j. Disconnect the CF connection between the 1.33" CF liquid feedthrough, glass vial, and custom Al adapter plate.
- k. Dispose of any remaining hfac in the ampoule as hazardous waste. Allow 30 minutes for any remaining hfac in the lines to evaporate in the fume hood, leaving the sash closed.
- l. Transfer the ampoule, allen wrench, replacement gasket, and fresh hfac into a glove box with inert atmosphere (Prof. Dunn's lab).
- m. Refill the ampoule, leaving about ½ inch below the steel-quartz joint for the doser tubing.
- n. Once ampoule is full, reconnect the 1.33" CF connection between the ampoule and the liquid feedthrough, then close both valves.
- o. Remove the ampoule from the glove box, ensuring that both valves are closed to prevent air from entering the ampoule.
- p. Mount the assembly back on the leg of the table, using zip ties to secure it.
- q. Reconnect V12 and V11 to the vapor chamber lines. V12 requires a stainless steel VCR gasket (do not use an Ag-plated gasket as it may corrode).
- r. Pressurize the ampoule with V11 (see step 12).

12. *Pressurize Ampoule*

- a. Open N₂ feed line valve (V7).
- b. Quickly open and close (~1s) V9 (for formic acid) or V11 (for hfac).
- c. Close V7.

13. *Empty Cold Trap:*

- a. To prevent the condensed etch product from entering the mechanical pump, as well as to preserve the product for further analysis, it is recommended to empty the cold trap before the system is turned off.
- b. Clear out an empty space in fumehood at north side of 1011, avoid conflict with other people's schedules.
- c. Close angle valve (AV).
- d. Turn off mechanical pump.
- e. Turn off cold trap, allow approximately 1 hour for ethylene glycol to raise temperature. Check periodically if the coldwell could be lifted.
- f. Wear glove and lab coat, make sure forearm is fully covered.

- g. Disconnect the two KF25 clamps on the coldwell.
- h. Lift the coldwell, use paper towel to wipe any ethylene glycol from the bottom of the Coldwell.
- i. Move the coldwell to the fumehood, open the 6'' sanitary clamp.
- j. Open the steel coldwell, fitting a jewelers flathead screwdriver underneath the cap will help with the removal but be careful not to damage the 6'' Viton gasket.
- k. Pull the cap straight up, be careful not to smash the underneath structure to the inner wall of the coldwell.
- l. If condensate does not need further analysis: use cleanroom wipe to absorb condensate, properly dispose the wipe after cleaning.
If condensate needs to be preserved for future analysis: use micropipet to move condensate to glass vials, clearly label experimental conditions on the vials. Clean up of the remaining condensate using cleanroom wipe and safely dispose the wipe.
- m. Reseal the cap, tighten the 6'' sanitary clamp.
- n. 800ml (~3.5 cm from the bottom of the well) of ethylene glycol is required in the cold trap for effective cooling. As taking out the coldwell also removes some ethylene glycol, refill ~50ml ethylene glycol into the cold trap before putting back the coldwell.
- o. Put the coldwell back into the cold trap, check the perimeter for proper sealing, use paper towel to clean up excessive ethylene glycol.
- p. Connect the two KF25 clamps, the taller stub connects to vapor chamber outlet, and the shorter stub connects to the mechanical pump inlet.
- q. Turn on mechanical pump.
- r. Open angle valve (AV).
- s. Turn on cold trap. Allow approximately 30 minutes for the cold trap to reach desired temperature (-50°C). Front panel LED should all light up.

14. *In Case of Chemical Spill:*

- a. In the event of a release of liquid hfac during the ampoule refill procedure, or formic acid or hfac vapor during the vapor delivery step, immediately alert any others working in room 1021 or 1011 and leave the area.
- b. If anyone was in contact with either acid, immediately wash the affected area for 15 minutes.
- c. To clean up a liquid formic acid spill, use excess acid neutralizer provided in the spill kit in room 1011 to neutralize the spill, then sweep up the waste, storing it for disposal be E&HS.
- d. Before cleaning a liquid hfac spill, wait for at least 30 minutes to let vapors from the spill dissipate.
- e. In the case of the release of formic acid or hfac vapors, immediately call 911 on the lab phone to inform E&HS and the fire dept., and do not re-enter the room until it has been cleared by E&HS.
- f. When disconnecting the formic acid ampoule or the hfac ampoule, caution must be exercised, as the lines that will be opened carry one of the liquids, and if not completely pumped out, can have residual formic acid or hfac remaining.

- g. Prior to disconnecting the lines to an ampoule, inform others working in room 1011 or 1021. Wear PPE (gloves, goggles, lab coat) and have cleanroom wipes ready in addition to the wrenches needed to open the lines.
- h. When opening a line that carries liquid, hold a cleanroom wipe around the fixture to soak up any residual liquid, and use your other hand to open the line slowly.

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