NACK NETWORK

For Nanotechnology Workforce Education

WWW.NANO4ME.ORG

Nanotechnology Applications

E SC 215

Unit 2
Material Fabrication Utilizing Dry Etch Chemistry

Lecture 2
Plasma Removal Process

Outline

- Introduction
- Models to understand the plasma process
- Chemistry
- Analyzing recipe parameters, and the resultant etch profiles
- Endpoint

Introduction

- Reactive Ion Etching (RIE): An etch process where a substrate is placed on an RF-powered electrode to achieve a chemical and physical etch
- Aspect Ratio: The ratio of the depth to width for a small gap, tech, or hole.
- DC Bias: A DC volt that develops across a plasma process chamber when an RF voltage is applied to the chamber's electrodes.
- Mean Free Path: The average distance an atom or molecule travels before striking another atom or molecule.
- Radicals: Molecules or fragments that contain unsatisfied bonds (unpaired electrons). They are extremely reactive.

Introduction

- <u>Ions:</u> Are atoms, molecules or pieces of molecules that have gained or lost electrons. They can be negatively (anions) or positively charged (cations).
- <u>Etch Rate</u>: The speed at which a material is removed from a substrate during etching
- <u>Residence Time</u>: The average time gas (etch chemistry, byproducts) is present in a vacuum chamber
- <u>Dark Sheath</u>: Area adjacent to plasma generating electrodes that appears darker than the rest of the plasma (glow region). The dark sheath (or ion sheath) is a result of a lack of electrons and has a stronger electric field as well as less resistance compared to the glow region
- <u>Sheath Potential</u>: The potential difference between the glow region of the plasma and the cathode in a dry etch system

Limits of Wet Etch Illustrates the Need for Plasma Processing

- Wet etching is limited to ~ 2-3 µm pattern features due to liquid trapping / surface tension (dependent upon materials)
- Wet etching tends to undercut and produce sloped sidewalls
- Wet etching needs rinse and dry steps
- Wet chemicals can be hazardous, toxic and expensive (environmental concerns)
- Wet processes present material contamination issues

Plasma Etching

- Plasma etching is a balance between:
  - Selective removal (what is intended vs. what is protected) of material through chemical reactions
  - Nonselective removal of material through ion bombardment (pressure and power related)
  - Deposition of sidewall polymers for passivation
  - Varying these parameters determines the etch profile

Plasma

- Within a plasma, there are a number of species
  - Radicals
  - Ions
  - Neutrals
  - Electrons
  - Film formers
    - if desired, for sidewall passivation in etch processes
  - Diluents

Contents of a Plasma

- A dry plasma etch may contain:
  - Radicals that chemically react with the substrate and **selectively** remove material
  - Ions that remove material through **physical bombardment** (no selectivity) and provide uniformity
  - Neutrals
  - Electrons aid in sustaining the plasma
  - Film formers that provide sidewall passivation (optional)
  - **Diluents**- an inert gas introduced into the reaction chamber along with the process gasses to maintain the desired reaction rate (optional)

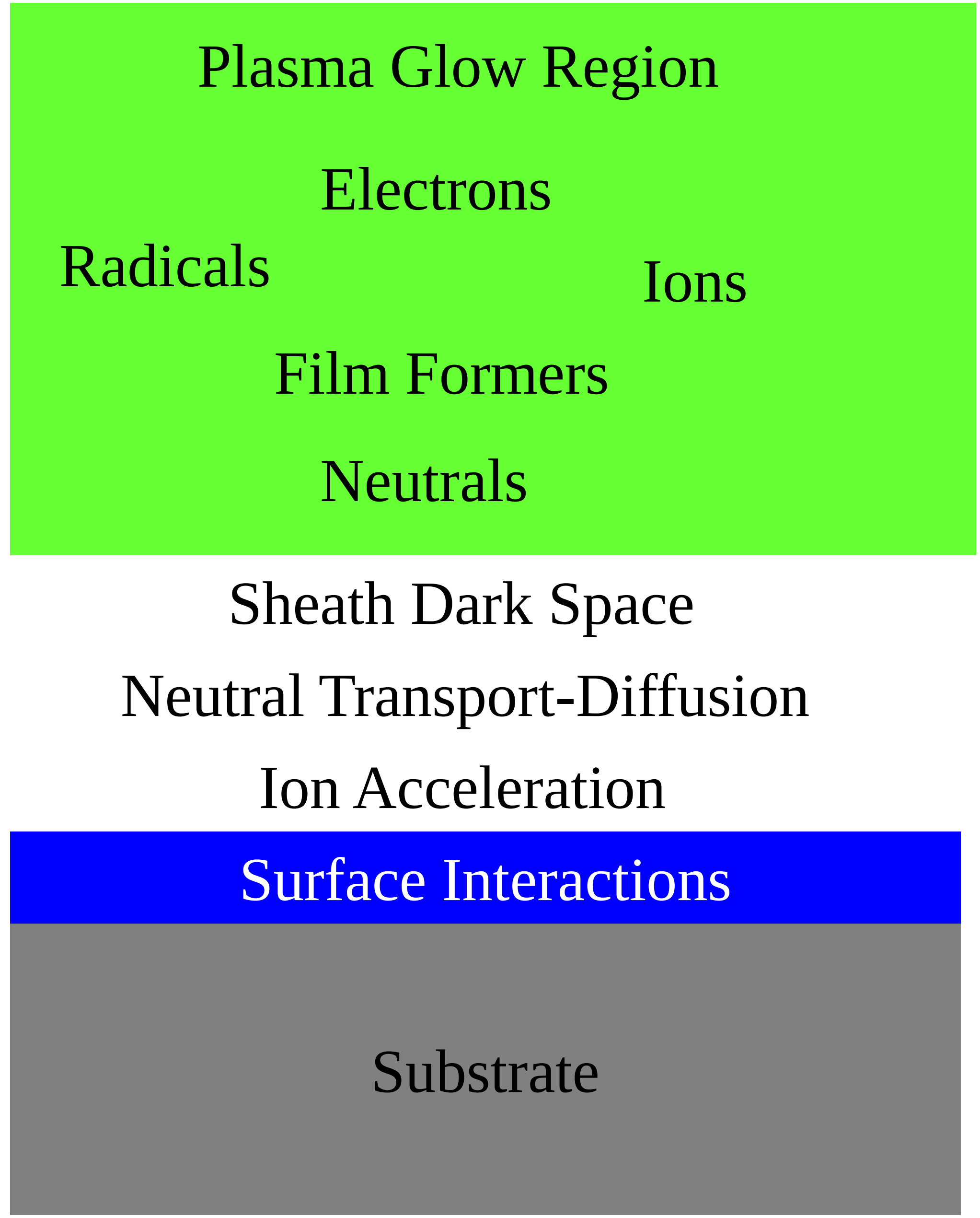
Selective Etching

- Etching that is done so that certain material is removed, but other materials or areas of the materials are ideally not affected
- Selective etching is difficult to achieve when chemically different layers form similar etch products
  - Example: SiO_2, Si, and Si_3N_4 each form SiF_4 during the etching process (↓ selectivity)

Outline

- Introduction
- Models to understand the plasma process
- Chemistry
- Analyzing recipe parameters, and the resultant etch profiles
- Endpoint

Simplified Plasma Model



Public Domain: Image Generated by CNEU Staff for free use

Ions vs. Radicals in a Plasma

- Radicals are molecules or pieces of molecules that contain unsatisfied bonds (unpaired electrons)
- Ions are molecules or pieces of molecules that are negatively or positively charged. We generally are concerned with the positive ions for focused bombardment, because they can be easily drawn to the cathode which holds the sample

Plasma in Terms of Temperature, Chemistry, and Bombardment

- Chemistry = Selectivity
  - Radicals react with surface to form volatile etch products that are pumped away
  - Selectivity, properly tuned chemistry can result in some materials being etched more than others
- Bombardment = Uniformity
  - Ions accelerated by the voltage difference between the plasma and the surface being etched strike the substrate and remove material by kinetic energy. Bombardment energy also aids surface chemical reactions. Bombardment is a power and pressure regulated process
- Temperature = Rate
  - Average plasma temperature (for a low density plasma) is about 100^{o}C plus room temperature, low enough for virtually any process, including photoresist
- Etch profile is a result of the energies at the substrate. C*B+T

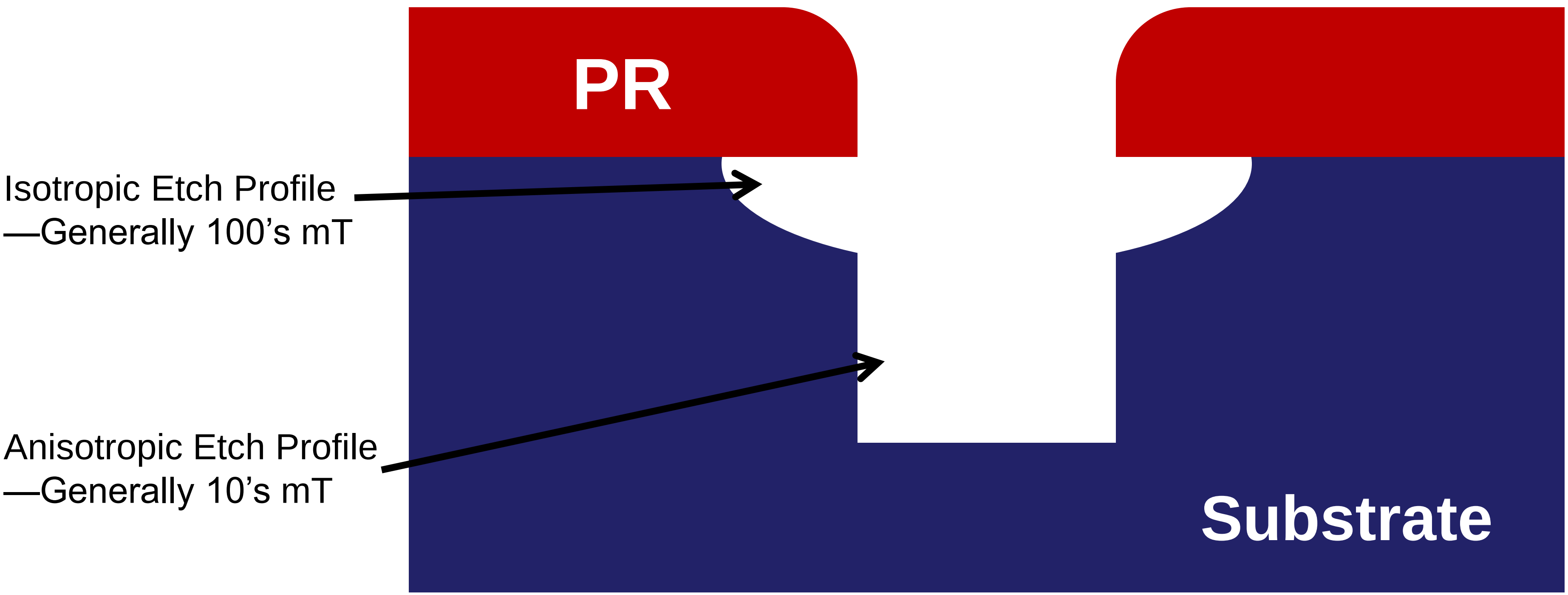
Pressure

- Pressure has the largest impact on plasma etching. It is the "big control knob"
- Pressure affects:
  - Mean free path (MFP)
  - Collisions at the material interface (substrate)
  - Etch profile: isotropic or anisotropic
  - Residence time
  - Microloading

Pressure

- Pressure affects the MFP, which controls, among other things, the degree of ionization and thus the number of ions available for physical bombardment
- MFP (bombardment) gets larger as pressure is reduced, naturally the amount of chemistry (etching gas, etch byproducts) is reduced when the pressure is decreased
- A low pressure will increase bombardment, and uniformity, but decrease selectivity
- A high pressure will decrease bombardment, and decrease uniformity, but will generally increase selectivity

The “Wine Glass” Etch Profile (RIE)



Public Domain: Image Generated by CNEU Staff for free use

Power

- Power also affects ionization
- As power increases, ionization increases
- Power and pressure are inter-related: the effect of power depends on the operating pressure.

Minimum Energy Required to Ionize a Particle

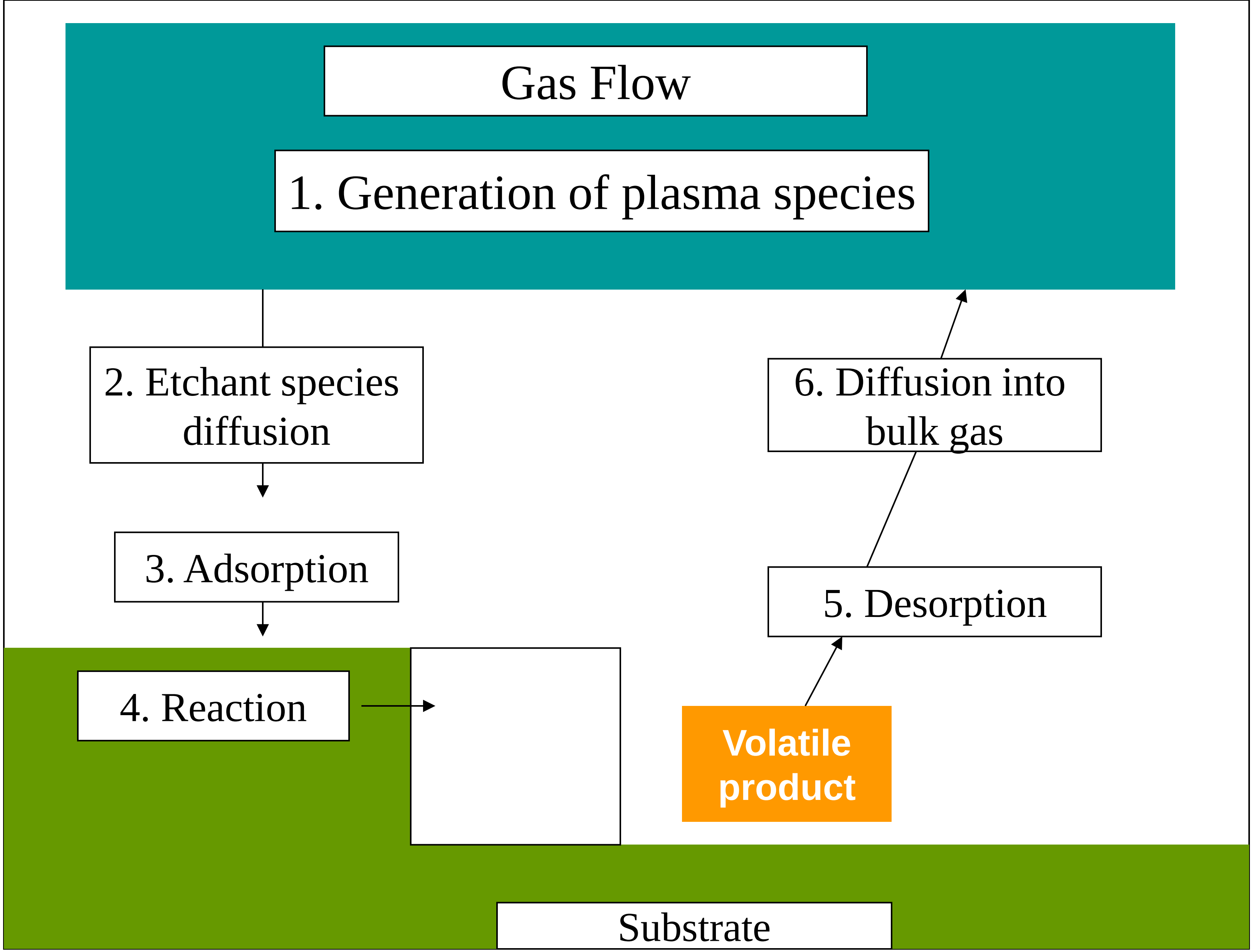
Particle	Energy(eV)	Particle	Energy(eV)
H	13.5	H_2	15.4
He	24.5	N_2	15.5
N	14.5	O_2	12.2
O	13.5	Cl_2	12
F	17.4	Br_2	11
Cl	13	BCl_3	11
Ar	15.7		

Process Variation Affects

- ↑**Power** = ↑Sheath potential ↑e^- velocity ↑Ions and radicals ↑Etch rate ↓Selectivity
- ↑**Pressure** = ↓Etch rate
- ↑**Area exposed to etching** = ↓Etch rate
- ↑**Electrode spacing =** ↓Ion energy ↓Ion density

The Six Steps of Plasma Etching

1. Reactive etching species are generated by electron/molecule collisions
2. Etchant species diffuse through stagnant region to the surface of the film to be etched
3. Etchant species adsorb onto surface (ion bombardment can help provide energy to drive chemical reactions)
4. Reaction takes place at the surface
5. Etched product desorbs from the surface (ion bombardment can help provide energy for desorption)
6. Etch products diffuse back into bulk gas and are removed by vacuum

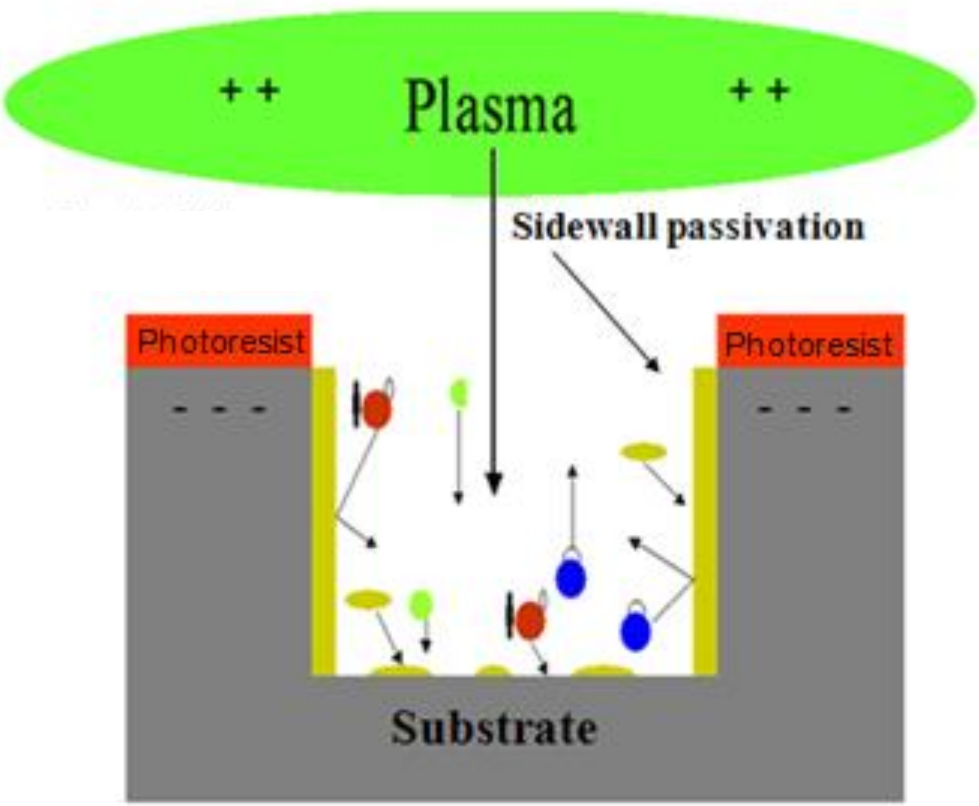


Public Domain: Image Generated by CNEU Staff for free use

Sidewall Passivation

- Sidewall passivation can be used in an etch process to control sidewall profile
- A film forms on the sidewalls, preventing the material from being etched isotropically
- The film is actually a polymer formed from the process gases and the photoresist layer on the substrate
- The polymers are basically combinations of carbon and hydrogen. May contain oxygen and nitrogen and other etch byproducts. Polymer chemistry depends on process conditions.
- Specific gases can be added to the recipe to insure passivation film formation

Etch Profile with Sidewall Passivation



Public Domain: Image Generated by CNEU Staff for free use

- **Radicals: reactive etching species**
- **Reaction Products: volatile etch products**
- **Film formers: provide sidewall passivation, photoresist can be a large contributor**
- **Positive ions: provide physical bombardment on surface, breaking surface film formers at bottom, physically etching and providing energy to help drive chemical reactions**

Sidewall Passivation

- Polymers coat the sidewalls and act as a "pseudo-mask" for protection from chemical attack
- Ions, for the most part, strike vertically and remove polymer buildup at the bottom of the etch
- The sidewall polymers are removed by using O_2 plasma at 500-750mT
  - This exposure uses a lot of chemistry and little bombardment

Outline

- Introduction
- Models to understand the plasma process
- Chemistry
- Analyzing recipe parameters, and the resultant etch profiles
- Endpoint

Controlling the Etch Process by Balancing Chemistry and Bombardment

- In dry etch processes choosing the correct chemistries can greatly increase the etch rate
- Increasing MFP of the plasma (decreasing the pressure) also increases the etch rate, this will aid uniformity
- Combining chemistry and bombardment will produce an etch rate that is greater than either contributor alone
- Combining chemistry and bombardment allows the profile to be “tuned” between isotropic and anisotropic
- The etch profile can also be enhanced with side wall passivation

Example Sidewall Chemistries

Material	Chemistry	Volatile Etch Product	Sidewall Material
Oxide Etch	$SiO_2 + CF_4 + CHF_3 + Ar \rightarrow$	SiF, SiOF, SiF_4, $SiH_4\uparrow$	Si, C, CH_x, F $\downarrow$
Poly Si Etch	$Si + HBr + Cl_2 \rightarrow$	$SiBr_x\uparrow$ $SiCl_x$	Si,Br,C,Cl $\downarrow$
Al Etch	$Al + BCl_3 + Cl_2 + N_2 \rightarrow$	$AlCl_3\uparrow$	Al,B,C,N,Cl $\downarrow$

Variations in Oxide Etch

Increase In:	Etch Rate of SiO_2	Selectivity to Silicon	Uniformity
Ion Energy	↑	↓	↑
O_2 Level in Process	↑	↓	↑
H_2 Level in Process	↓	↑	↓
SiO_2 Dopant Level	↑	↑	↓
Silicon Dopant Level		↓	

Some etching Gases

Formula	Common Name	Chemical Name	Formula	Chemical Name
CF_4	Freon 14	Tetrafluoro-methane	$SiCl_4$	Silicon Tetrachloride
C_2F_6	Freon 116	Perfluoro-ethane	BCl_3	Boron-trichloride
C_3F_8	Freon 218	Perfluoro-propane	Cl_2	Chlorine
CHF_3	Freon 23	Trifluoro-methane	HCl	Hydrogen Chloride
CF_3Br	Freon 13B1	Bromo-trifluoro-methane	HBr	Hydrogen Bromide
SF_6		Sulfur Hexafluoride	He	Helium
NF_3		Nitrogen Trifluoride	N_2	Nitrogen
SiF_4		Silicon Tetrafluoride	O_2	Oxygen

Some Materials and Selected Etchants

Material	Chemistry	Material	Chemistry
PolySilicon	Cl_2 or BCl_3/CCl_4 HBr /CF_4 /$CHCl_3$ /CHF_3	WSi_2,$TiSi_2$,$CoSi_2$	CCl_2F_3
Aluminum	Cl_2 BCl_3 + passivating gases $SiCl_4$	Single crystal Si	Cl_2 or BCl_3 + passivating gases
AlSi(1%)-Cu(0.5%)	same as Al	SiO_2 (BPSG)	CCl_2F_2,CF_4,C_2F_6, C_3F_8
Al-Cu(2%)	$BCl_3/Cl_2/CHF_3$	Si3N4	CCl_2F_2 CHF_3
Tungsten	$SF_6/Cl_2/CCl_4$	GaAs	CCl_2F_2
TiW	$SF_6/Cl_2/O_2$		

Outline

- Introduction
- Models to understand the plasma process
- Chemistry
- Analyzing recipe parameters and the resultant etch profiles
- Endpoint

The “Egg” Chart

- This analytical model is a graphical representation of various process parameters. The Y axis represents bombardment energy, the X axis represents chemical energy, and the “dog leg” boundary represents polymer formation.
- For an ideal anisotropic etch, the required parameter zone resembles an “egg” in the middle of the chart
- This chart shows the combined effects of chemistry, bombardment, and polymerization (C*B+P) to predict sidewall profiles
- There are also other factors that determine the etch profile that are not included in this exercise. These parameters will be discussed after this first iteration analysis.

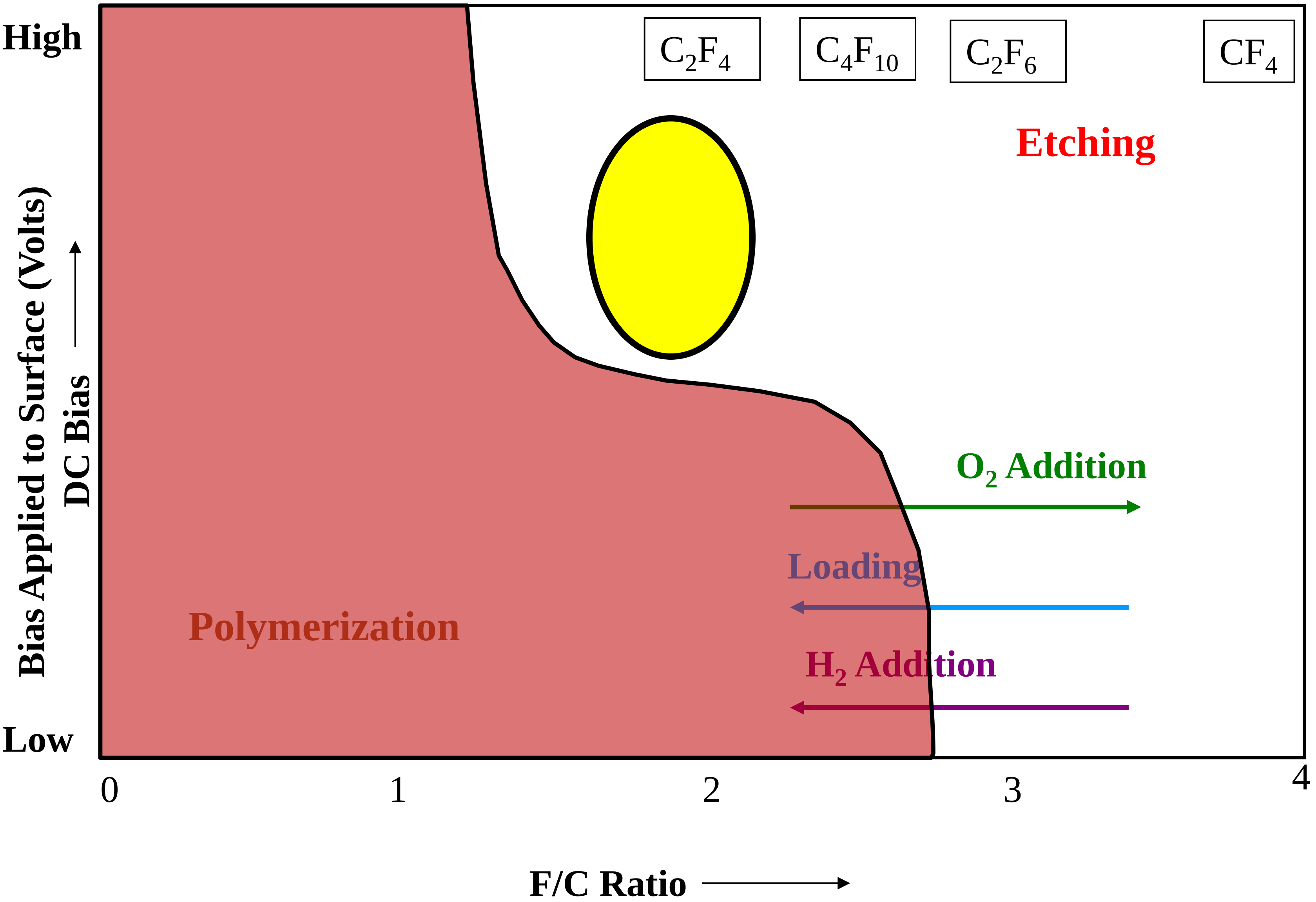
The “Egg” Chart

- A chart like this can be found and/or generated for any dry etchable material
- Due to its wide use in micro and nanofabrication, we will analyze the egg chart for SiO_2
- Naturally this chart is not “exact”, but can be used as a starting point for building a etch recipe.

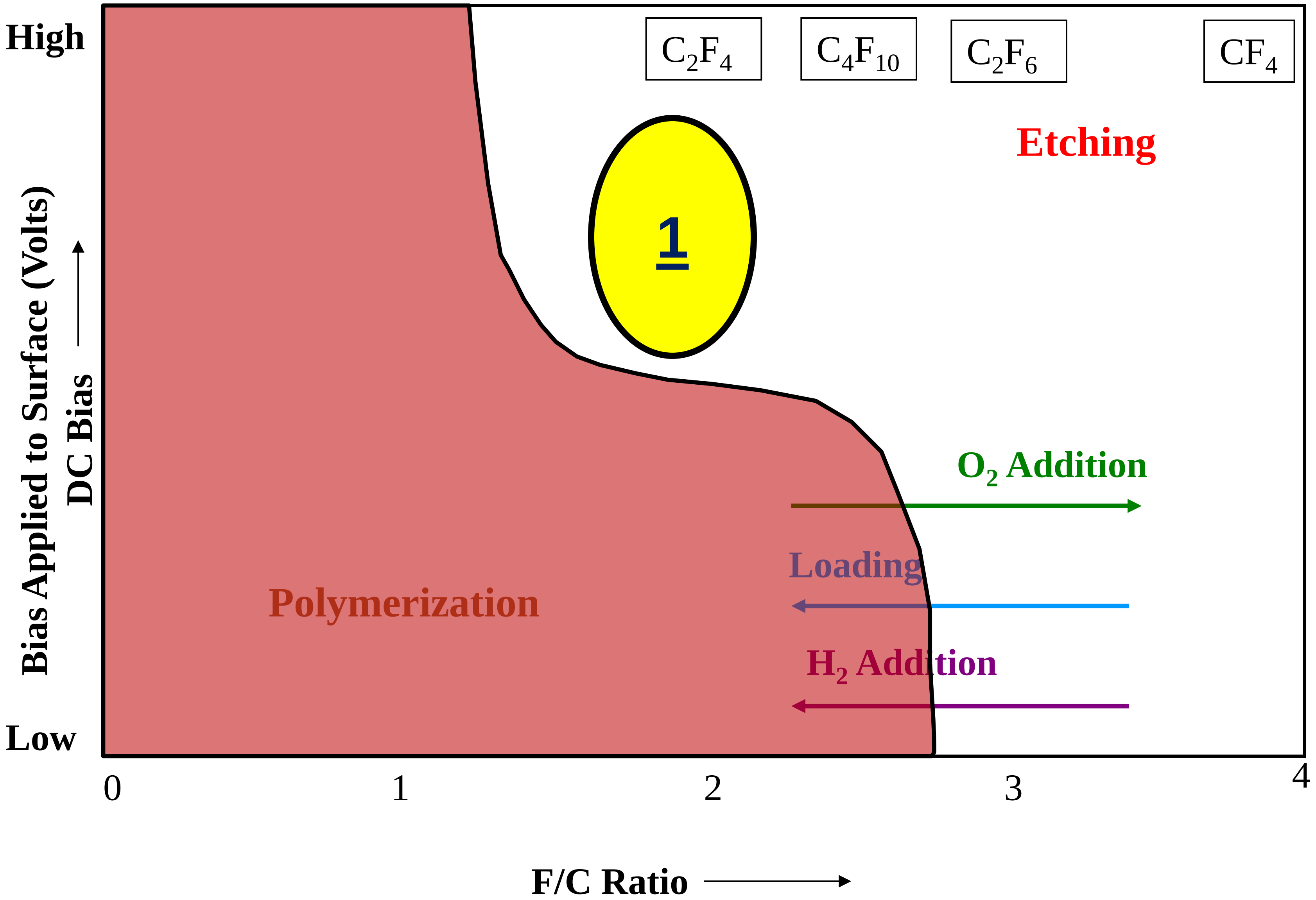
Oxide Egg Chart Considerations

- F/C Ratio- the ratio of fluorine to carbon etching species
- Increasing DC bias, increases bombardment
- The addition of H_2 to the chamber increases polymerization
- The addition of O_2 to the chamber increases free fluorine
- Aspect Ratio- the ratio of depth to width for a small gap, trench, or hole

Fluorine to Carbon Ratio (F/C) of Gas Phase Etching Species vs DC Bias Level



Fluorine to Carbon Ratio (F/C) of Gas Phase Etching Species vs DC Bias Level

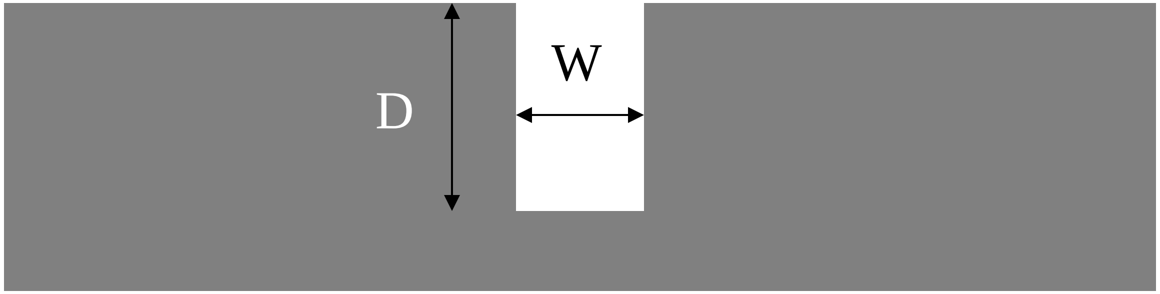


Public Domain: Image Generated by CNEU Staff for free use

The Ideal Profile

- To be “in the egg” is to achieve the ideal anisotropic etch
  - The ideal F/C ratio is approximately 2
  - An equal mix of hydrogen and oxygen to balance polymerization and etch
  - DC bias level that provides just enough bombardment

The Ideal Profile

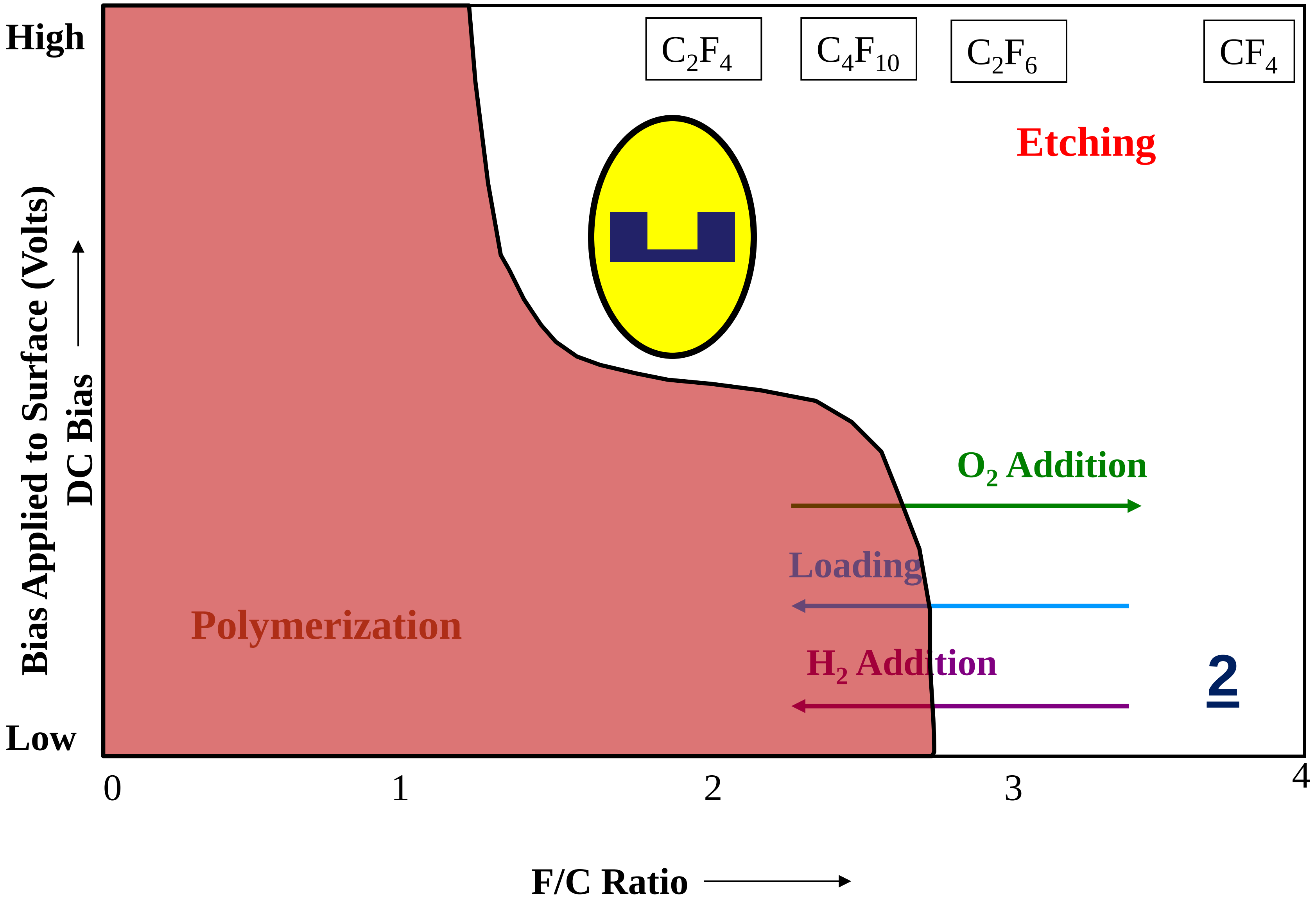


Public Domain: Image Generated by CNEU Staff for free use

Sidewall Profile Two

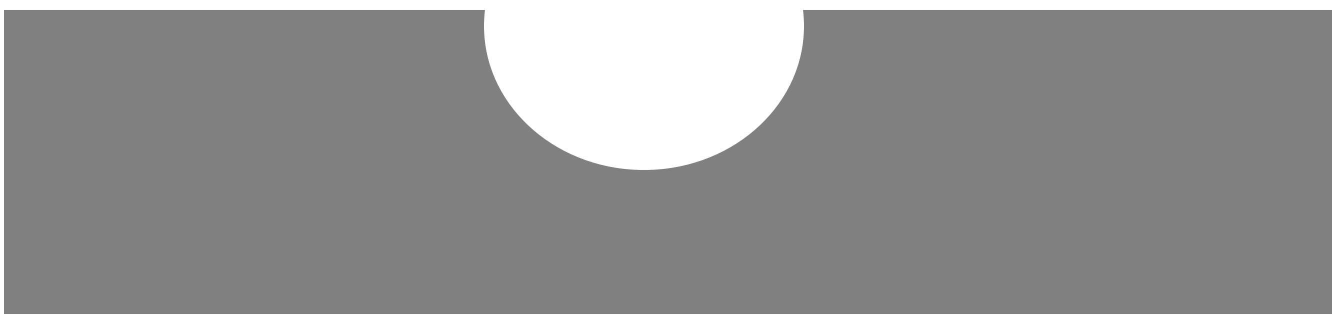
- Low DC bias – little/no bombardment
- No H_2 - no polymerization
- A lot of O_2 – can increase etching
- F/C ratio = 4, SiF_4 is formed
- Aspect ratio < 1, an isotropic etch profile

Fluorine to Carbon Ratio (F/C) of Gas Phase Etching Species vs DC Bias Level



Public Domain: Image Generated by CNEU Staff for free use

Sidewall Profile Two

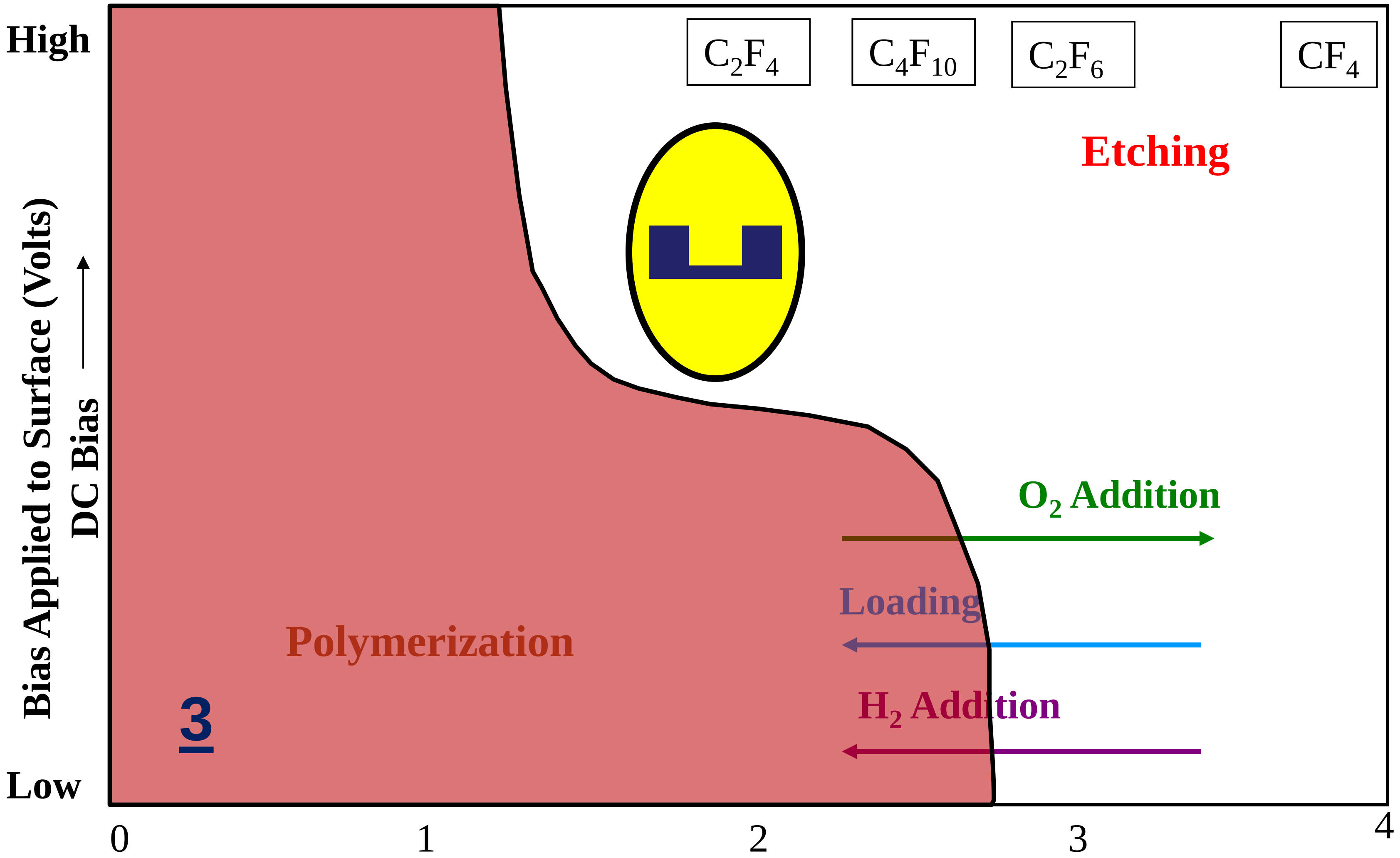


Public Domain: Image Generated by CNEU Staff for free use

Sidewall Profile Three

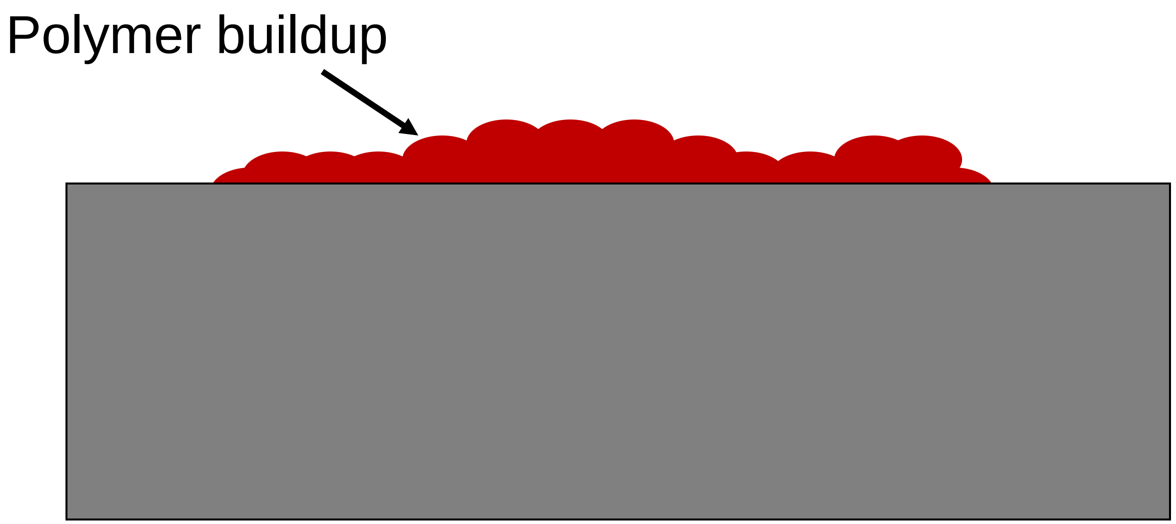
- Low DC bias – no bombardment
- A lot of H_2 - a lot of polymerization
- No O_2 – no etch
- F/C = $^1/_3$, SiF_4 is not formed

Fluorine to Carbon Ratio (F/C) of Gas Phase Etching Species vs DC Bias Level



Public Domain: Image Generated by CNEU Staff for free use

Sidewall Profile Three

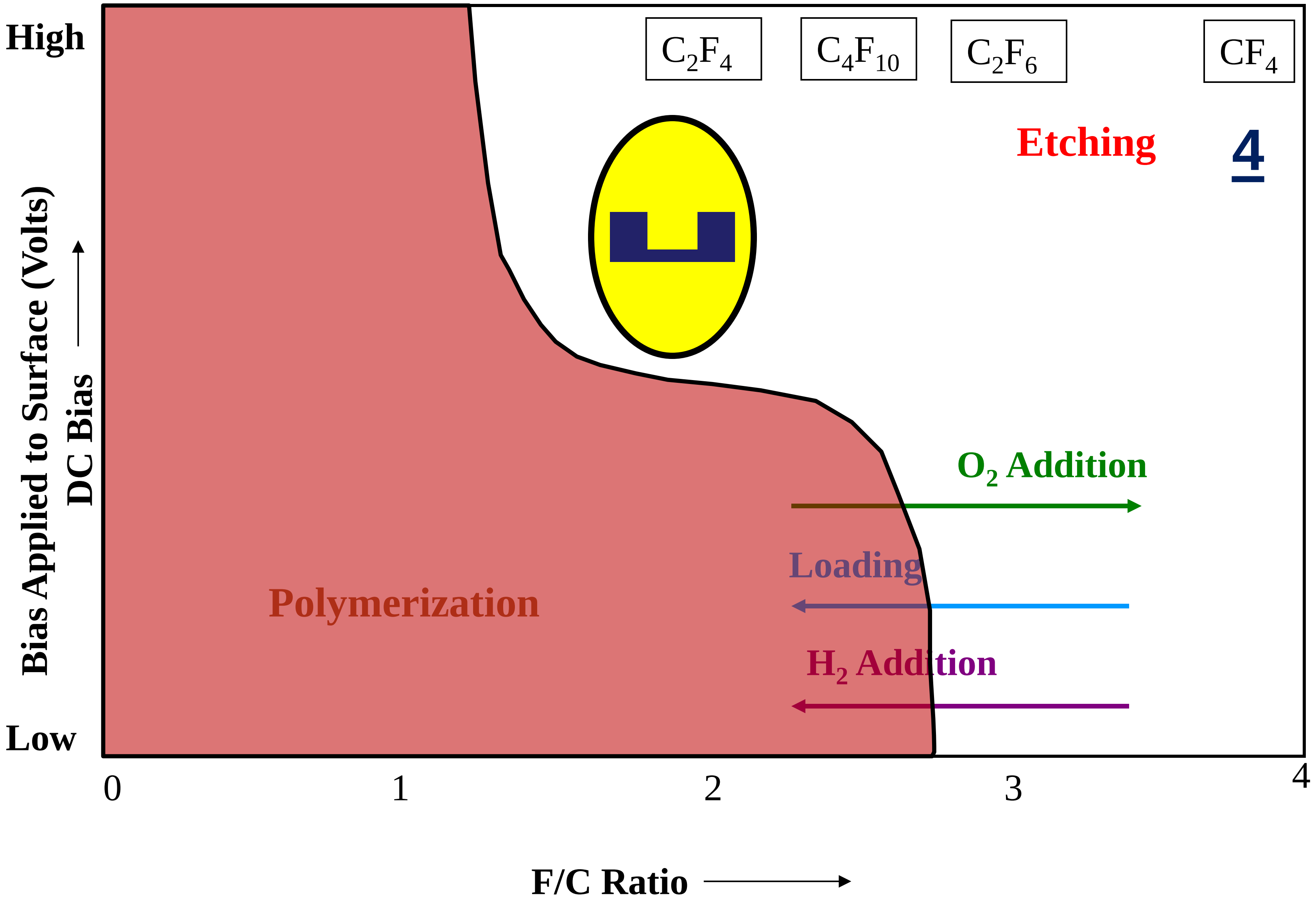


Public Domain: Image Generated by CNEU Staff for free use

Sidewall Profile Four

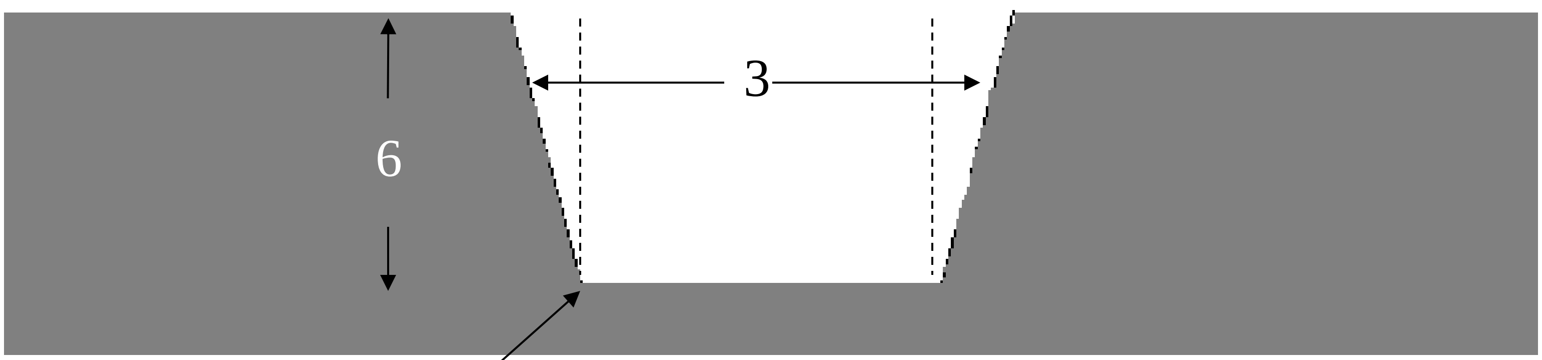
- High DC bias – high bombardment
- No H_2 – no polymerization
- A lot of O_2 – high etch
- F/C ratio = 4, SiF_4 is formed
- Aspect ratio >1, a dry etch profile

Fluorine to Carbon Ratio (F/C) of Gas Phase Etching Species vs DC Bias Level



Public Domain: Image Generated by CNEU Staff for free use

Sidewall Profile Four



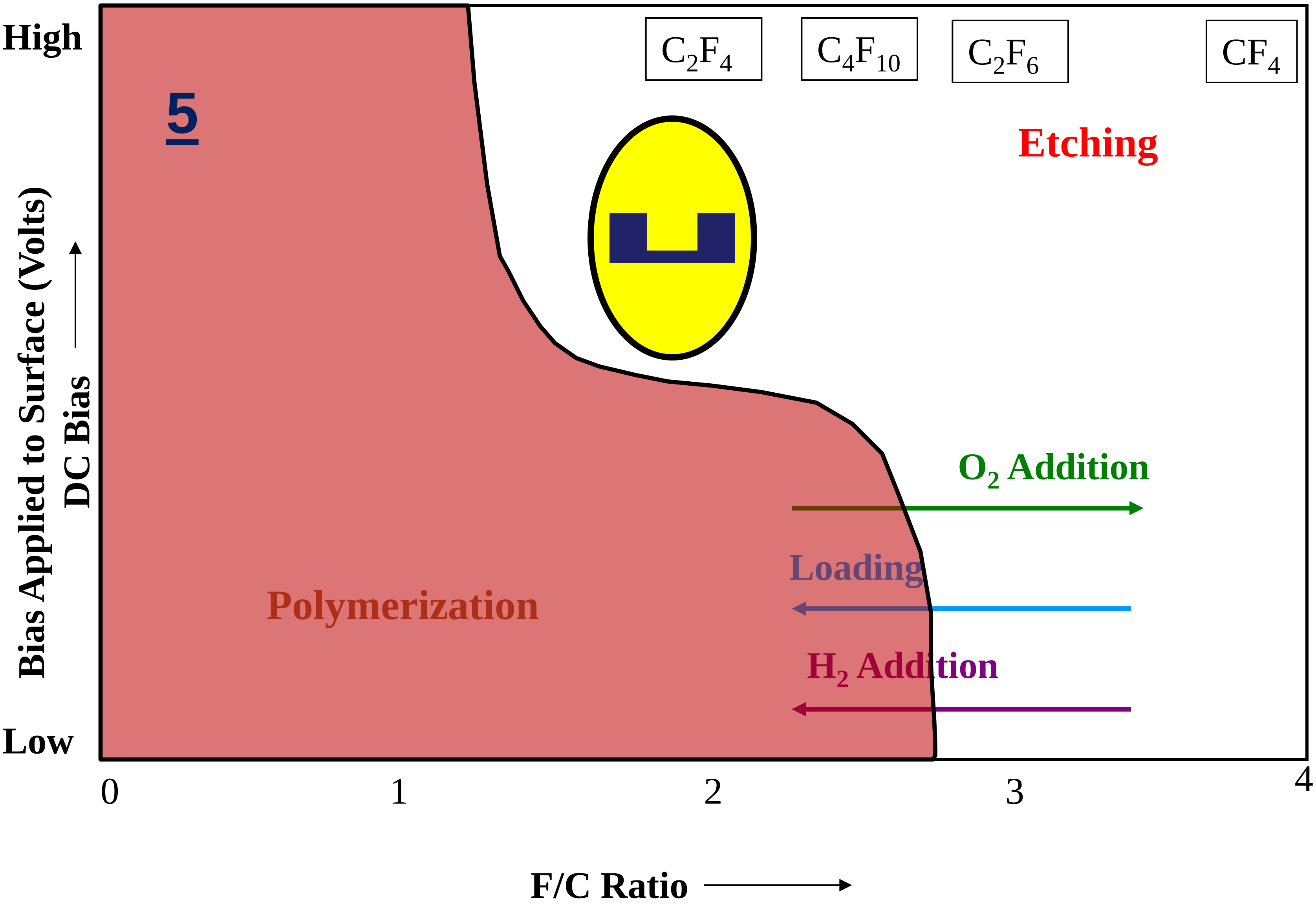
Sharp angles due
to high bombardment
with no polymerization

Public Domain: Image Generated by CNEU Staff for free use

Sidewall Profile Five

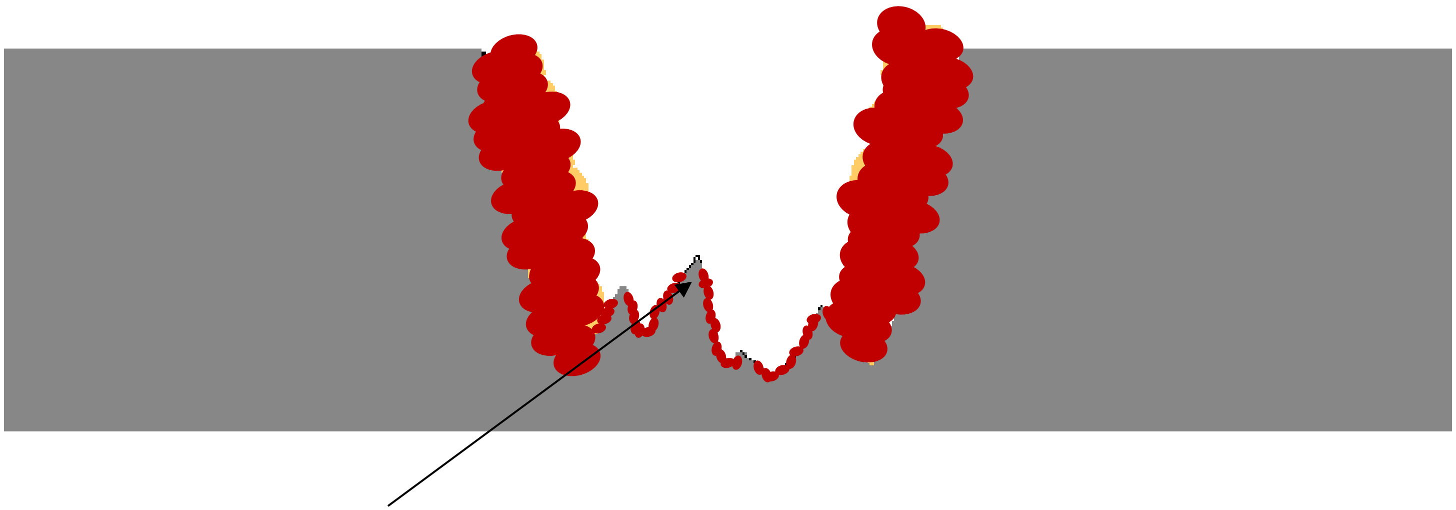
- High DC bias – high bombardment
- A lot of H_2 – a lot of polymerization
- No O_2 – no etch
- F/C ratio $= {}^{1}/_{5}$, SiF_4 is not formed
- Aspect ratio > 1, Dry etch profile with undesirable features

Fluorine to Carbon Ratio (F/C) of Gas Phase Etching Species vs DC Bias Level



Public Domain: Image Generated by CNEU Staff for free use

Sidewall Profile Five

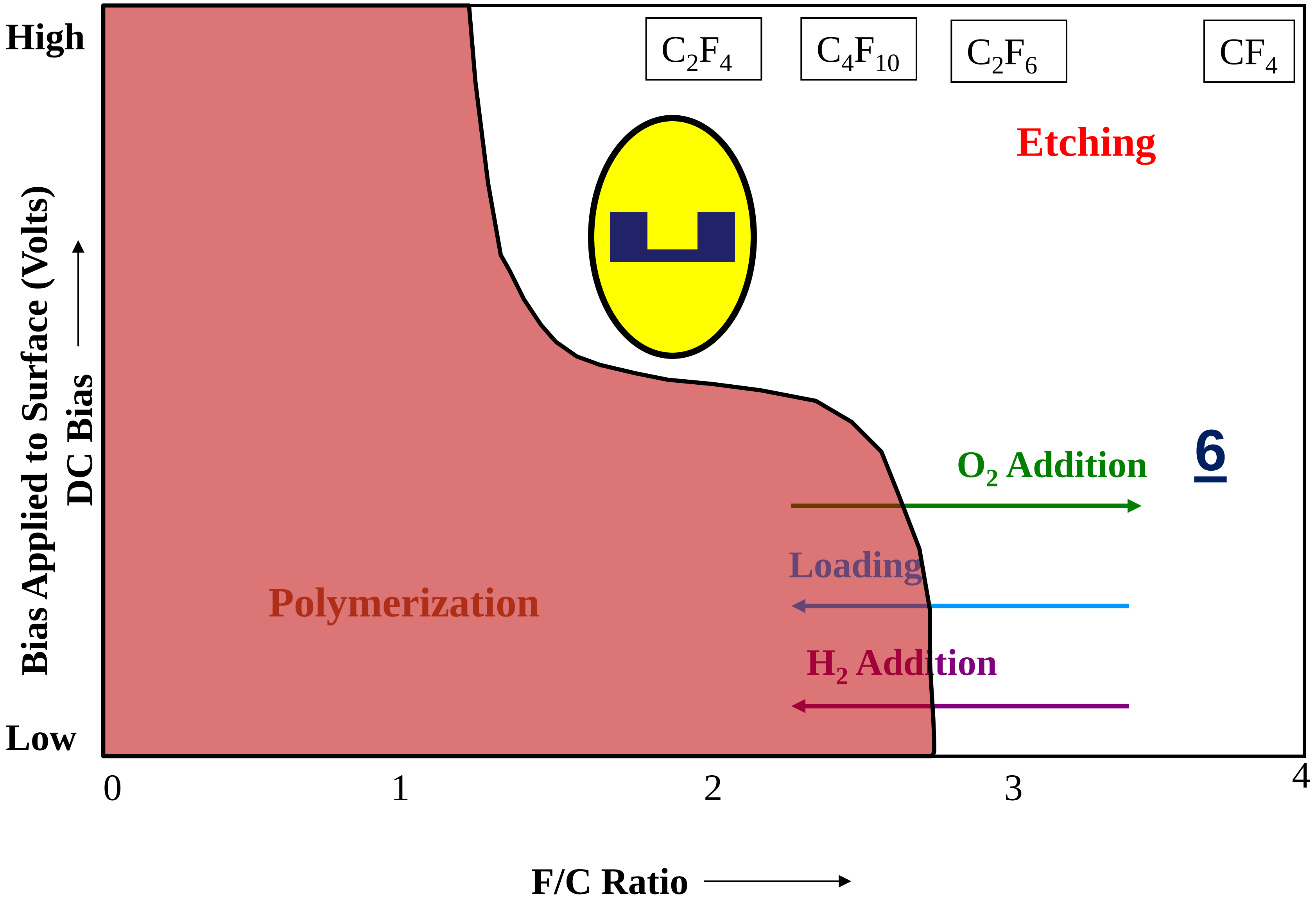


Public Domain: Image Generated by CNEU Staff for free use

Sidewall Profile Six

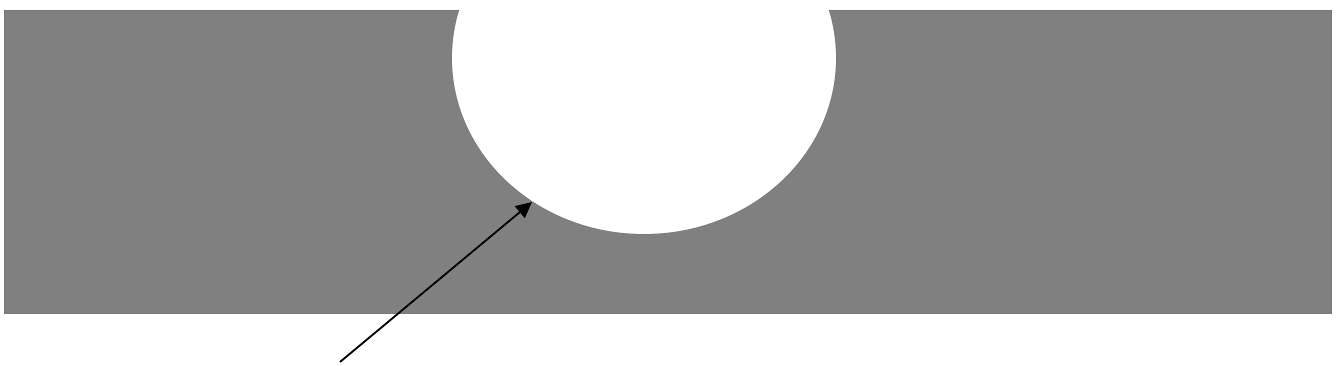
- Medium DC bias – medium bombardment
- No H_2 – no polymerization
- A lot of O_2 – high etch
- $F/C = 4$, SiF_4 is formed
- Aspect ratio < 1, a wet etch profile

Fluorine to Carbon Ratio (F/C) of Gas Phase Etching Species vs DC Bias Level



Public Domain: Image Generated by CNEU Staff for free use

Sidewall Profile Six



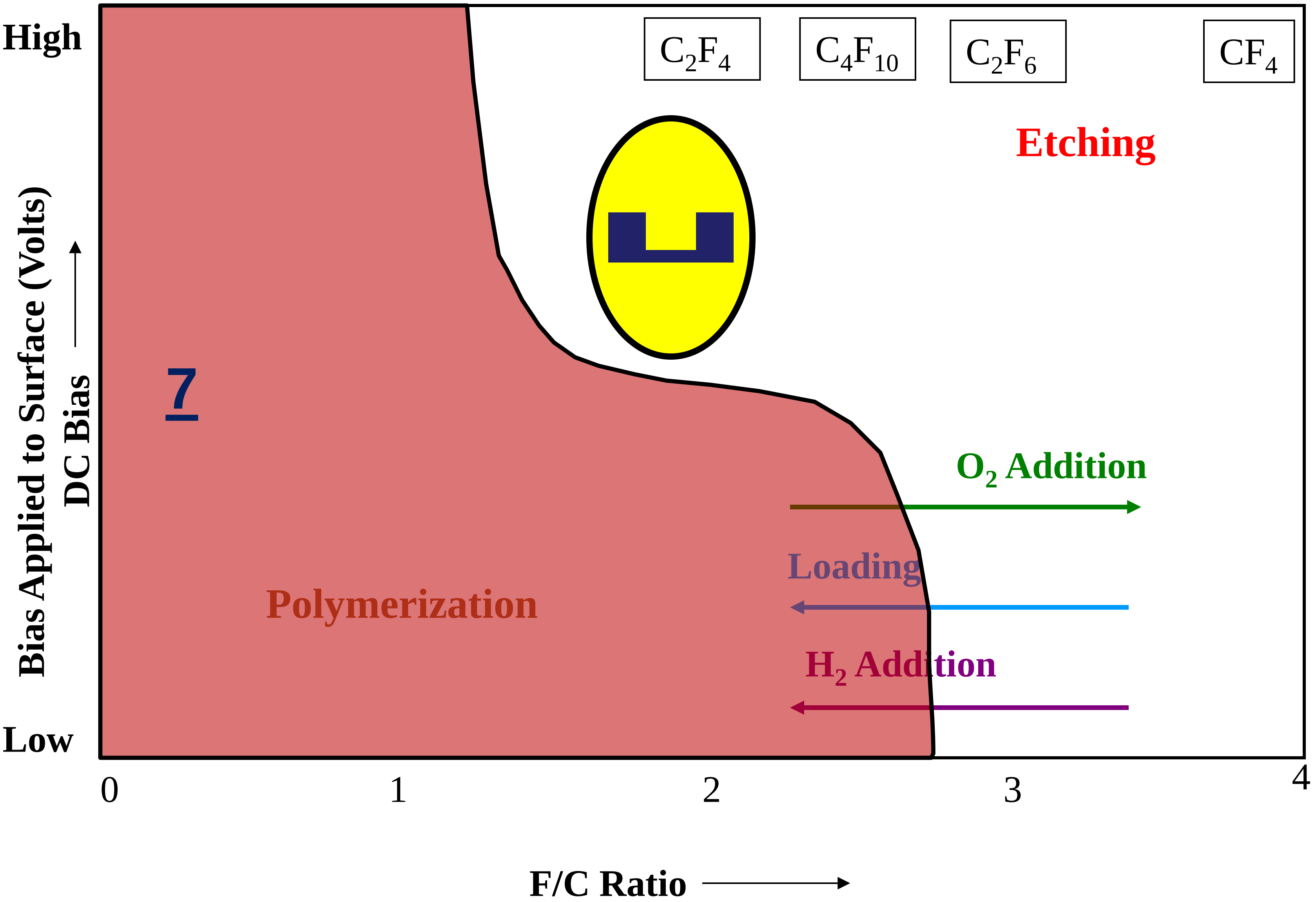
Wider and deeper than profile one due to increased bombardment

Public Domain: Image Generated by CNEU Staff for free use

Sidewall Profile Seven

- Medium DC bias – medium bombardment
- A lot of H_2 – a lot of polymerization
- No O_2 – no etch
- F/C ratio = ¼, SiF_4 is not formed
- Aspect ratio > 1, Dry etch profile with undesirable features

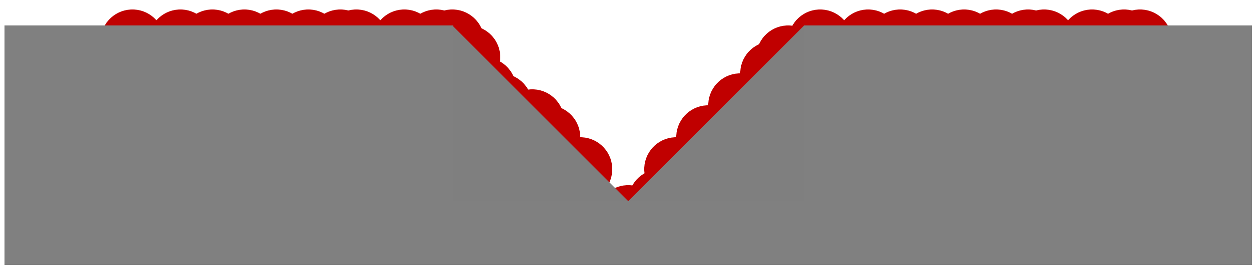
Fluorine to Carbon Ratio (F/C) of Gas Phase Etching Species vs DC Bias Level



Public Domain: Image Generated by CNEU Staff for free use

Sidewall Profile Seven

Less bombardment than profile four



Public Domain: Image Generated by CNEU Staff for free use

Considerations Beyond the Egg Chart

- The "egg chart" is a useful first approximation to define some process parameters, but it does not cover some important considerations.
- We will discuss 4 additional considerations:
  - Residence time
  - Microloading
  - Proximity effect
  - Post etch evaluation

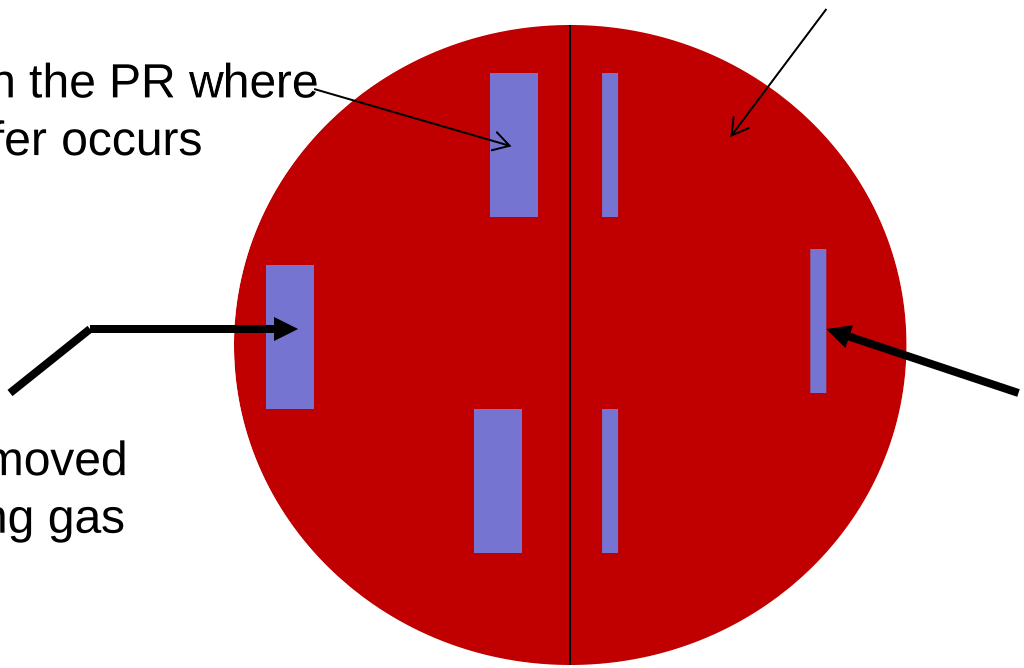
Residence Time

- The average time gas is present in the chamber (seconds)
- The residence time is a balance of the pressure, input gas flow, and the pump efficiency
- Naturally the residence time will impact the etch process, because etch chemistry and byproducts are constantly being pumped away at a certain rate

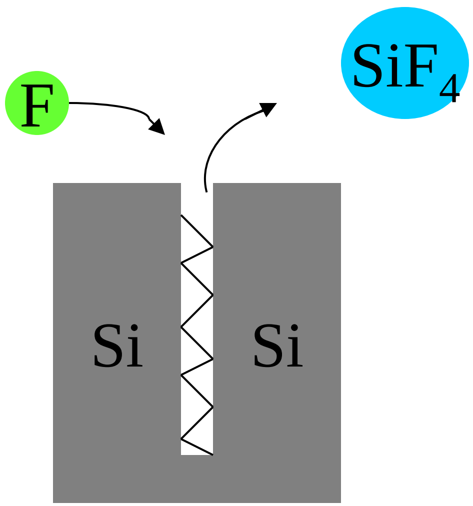
Microloading

- The change in local etch rate relative to the whole area of material being etched
  - A large area will load the etching process with volatile etch products, slowing the etch down in that area while a smaller etch area proceeds at a faster rate
- Etch rates change according to pattern and exposed area

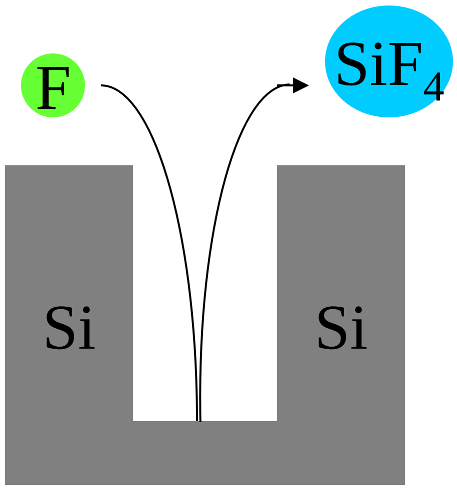
Microloading



Proximity Effect- Etch Rate Based on Feature Size



"Crowded"-
harder to remove byproducts,
slower etch rate



Easier to remove byproducts,
faster etch rate

Public Domain: Image Generated by CNEU Staff for free use

Etch Evaluation

- Process quality parameters:
  - Etch rate, selectivity, uniformity
  - Sidewall Profile
  - Loss or gain of critical dimensions
  - Corrosion (in metal etch)
  - Reproducibility

Outline

- Introduction
- Models to understand the plasma process
- Chemistry
- Analyzing recipe parameters, and the resultant etch profiles
- Endpoint

Endpoint Detection

- General term describing when an etch process has finished
- Two common methods of detection
  - Optical emission
  - Mass spectroscopy

Optical Emission

- Each volatile etch product emits a specific wavelength
- The wavelength intensity shows the relative amounts of products being formed
- A decrease in intensity corresponds to a decrease in etch products.

RIE With Optical Endpoint Detector

Endpoint Detector

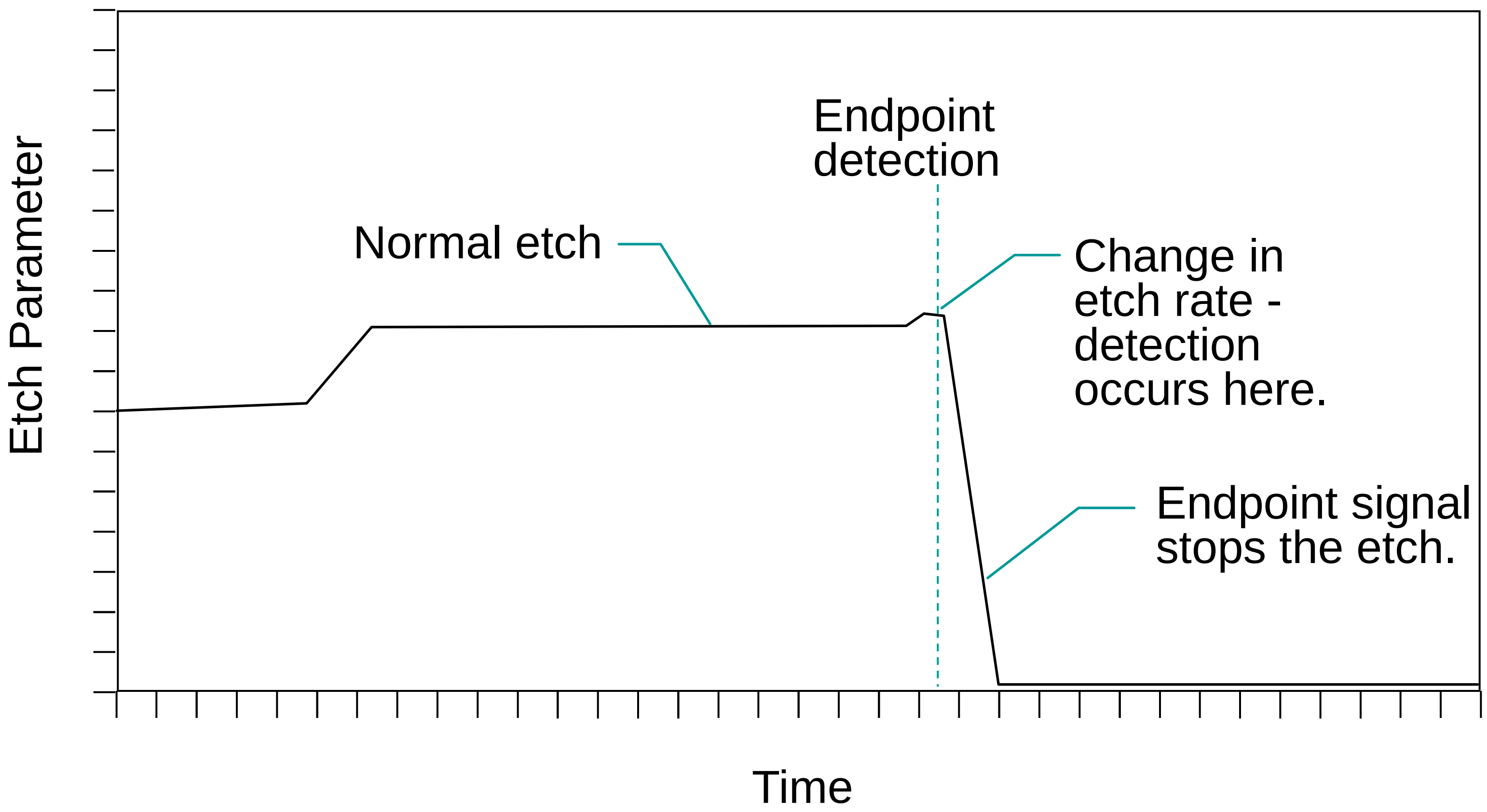
Oxford Instruments Plasmalab System 100

Public Domain: Image Generated by CNEU Staff for free use

Optical Emission

Material to be etched	Etchant Gases	Emitting Species	**λ(nm)**
Silicon	CF_4/O_2;SF	F(product)	704
	CF_4/O_2;SF	SiF(product)	440,777
	Cl_2	SiCl(product)	287
SiO_2	CHF_3	CO(product)	484
Si_3N_4	CF_4/O_2	N_2(product)	337
	CF_4/O_2	CN(product)	387
	CF_4/O_2	N(product)	674
	CF_4/O_2	F(etchant)	704
Al	Cl_2;BCl_3	Al(product)	
391,394,396			
	Cl_2;BCl_3	AlCl(product)	261
Resist	O_2	O(etchant)	777,843
	O_2	CO(product)	484
	O_2	OH(product)	309
	O_2	H(product)	656

Example Graph of Optical Endpoint Detection

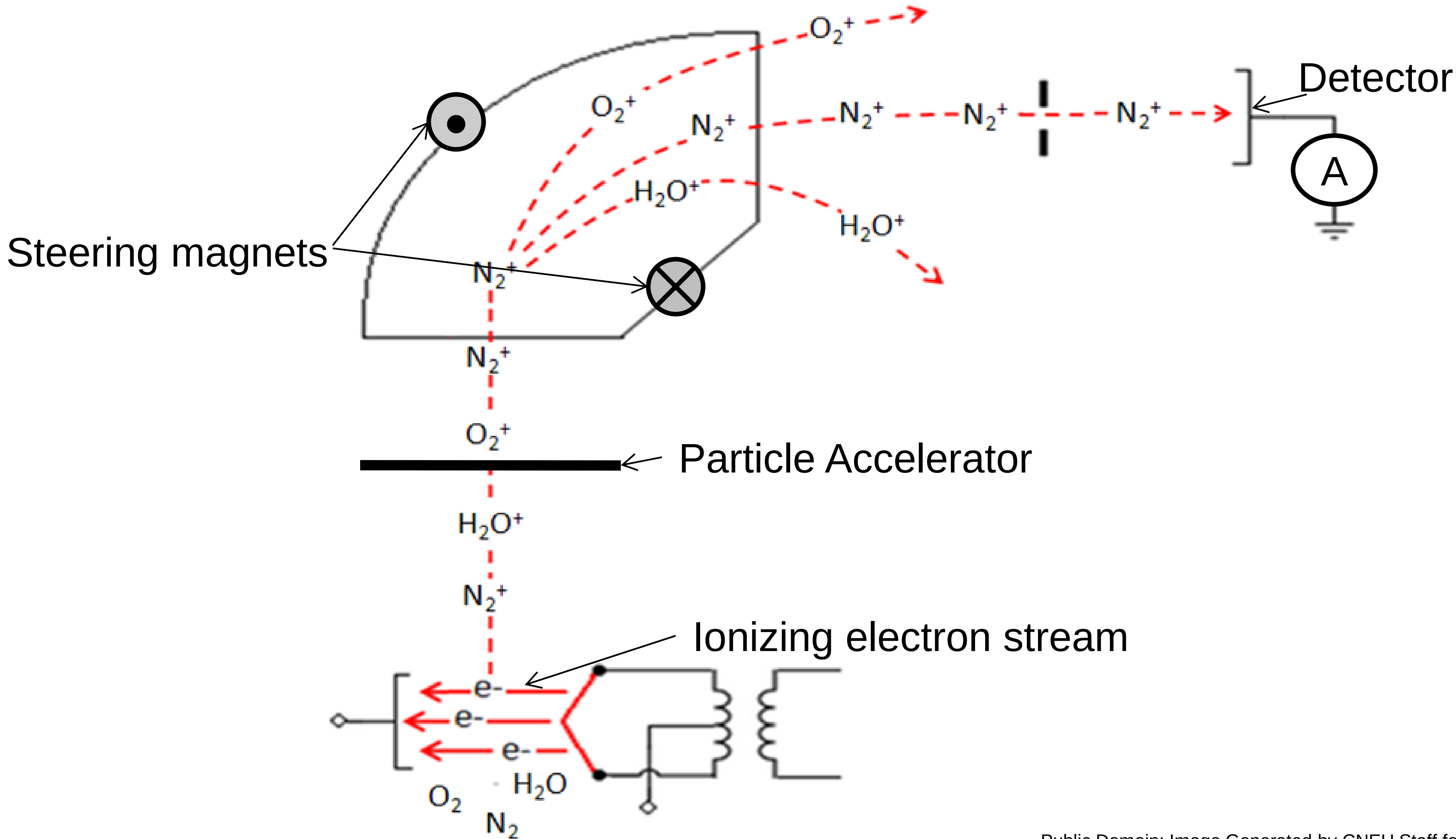


Public Domain: Image Generated by CNEU Staff for free use

Mass Spectroscopy

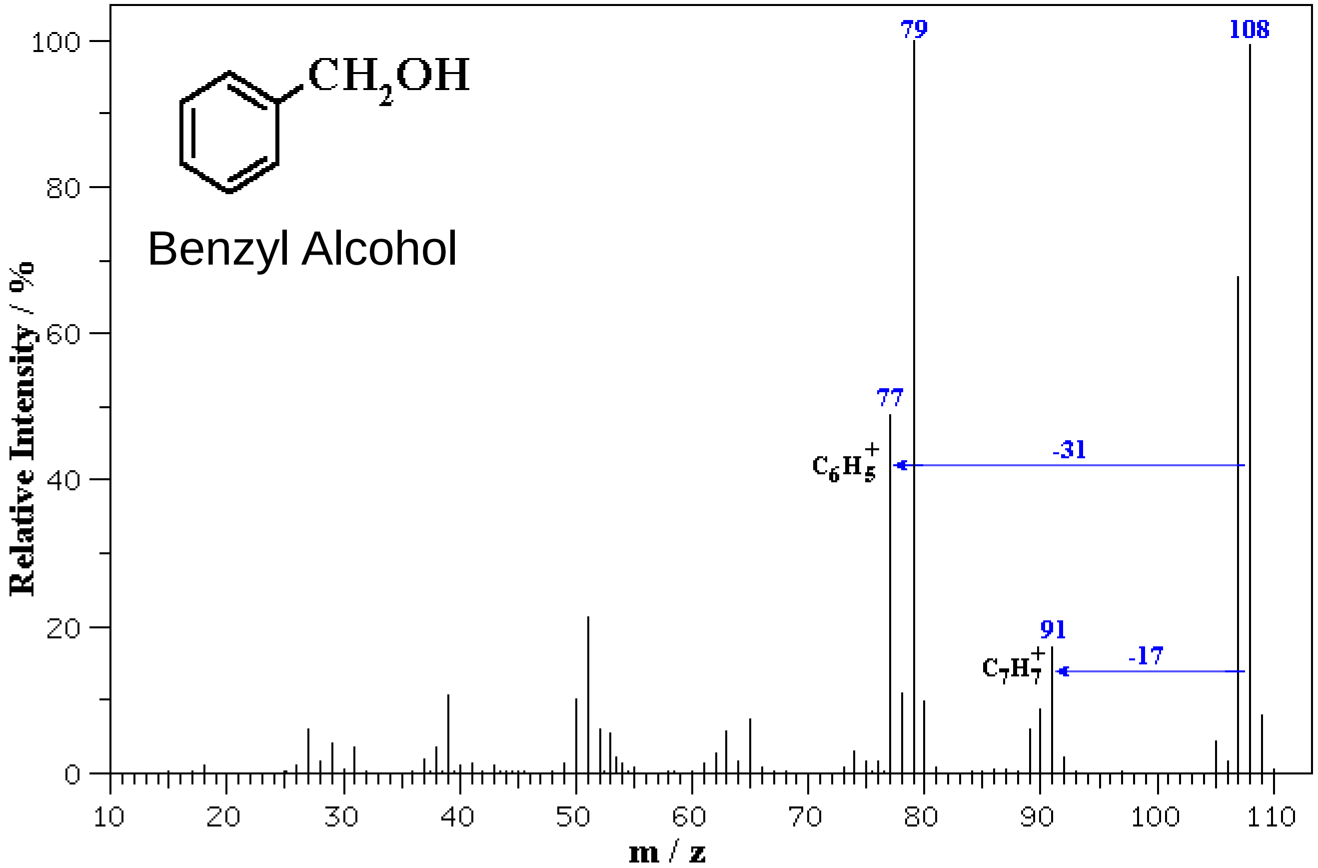
- This method of endpoint detection measures the mass/charge ratio of the etch products
- As the mass/charge ratio peak declines, the products being generated by the etch decline due to the material being etched away
- A residual gas analyzer is a mass spectrometer

Mass Spectrometer Schematic



Public Domain: Image Generated by CNEU Staff for free use

Example Mass Spectra: Benzyl Alcohol



Public Domain: Image Generated by CNEU Staff for free use