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Workforce Development

# Plasma Removal Process

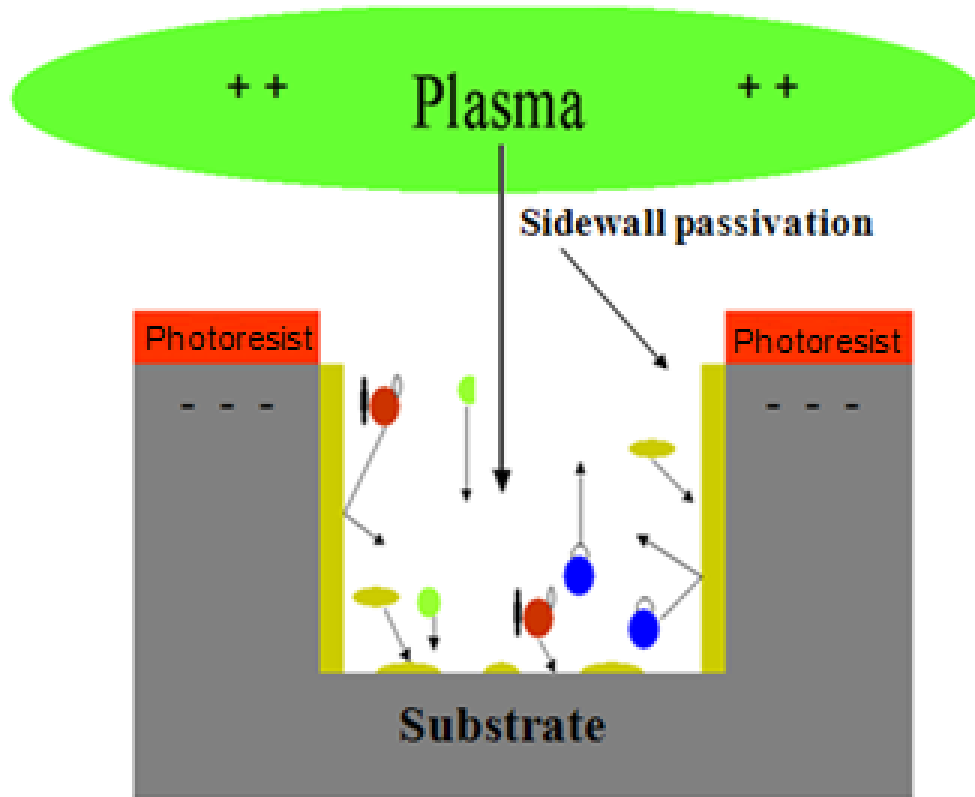
# Outline

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





# 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



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-  **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

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# 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	$\text{SiO}_2 + \text{CF}_4 + \text{CHF}_3 + \text{Ar} \rightarrow$	$\text{SiF}$ , $\text{SiOF}$ , $\text{SiF}_4$ , $\text{SiH}_4 \uparrow$	$\text{Si}$ , $\text{C}$ , $\text{CH}_x$ , $\text{F} \downarrow$
Poly Si Etch	$\text{Si} + \text{HBr} + \text{Cl}_2 \rightarrow$	$\text{SiBr}_x \uparrow$ $\text{SiCl}_x$	$\text{Si}$ , $\text{Br}$ , $\text{C}$ , $\text{Cl} \downarrow$
Al Etch	$\text{Al} + \text{BCl}_3 + \text{Cl}_2 + \text{N}_2 \rightarrow$	$\text{AlCl}_3 \uparrow$	$\text{Al}$ , $\text{B}$ , $\text{C}$ , $\text{N}$ , $\text{Cl} \downarrow$



# Some etching Gases

Formula	Common Name	Chemical Name	Formula	Chemical Name
$\text{CF}_4$	Freon 14	Tetrafluoro-methane	$\text{SiCl}_4$	Silicon Tetrachloride
$\text{C}_2\text{F}_6$	Freon 116	Perfluoro-ethane	$\text{BCl}_3$	Boron-trichloride
$\text{C}_3\text{F}_8$	Freon 218	Perfluoro-propane	$\text{Cl}_2$	Chlorine
$\text{CHF}_3$	Freon 23	Trifluoro-methane	$\text{HCl}$	Hydrogen Chloride
$\text{CF}_3\text{Br}$	Freon 13B1	Bromo-trifluoro-methane	$\text{HBr}$	Hydrogen Bromide
$\text{SF}_6$		Sulfur Hexafluoride	$\text{He}$	Helium
$\text{NF}_3$		Nitrogen Trifluoride	$\text{N}_2$	Nitrogen
$\text{SiF}_4$		Silicon Tetrafluoride	$\text{O}_2$	Oxygen

# Some Materials and Selected Etchants

Material	Chemistry	Material	Chemistry
PolySilicon	Cl <sub>2</sub> or BCl <sub>3</sub> /CCl <sub>4</sub> HBr /CF <sub>4</sub> /CHCl <sub>3</sub> /CHF <sub>3</sub>	WSi <sub>2</sub> , TiSi <sub>2</sub> , CoSi <sub>2</sub>	CCl <sub>2</sub> F <sub>3</sub>
Aluminum	Cl <sub>2</sub> BCl <sub>3</sub> + passivating gases SiCl <sub>4</sub>	Single crystal Si	Cl <sub>2</sub> or BCl <sub>3</sub> + passivating gases
AlSi(1%)-Cu(0.5%)	same as Al	SiO <sub>2</sub> (BPSG)	CCl <sub>2</sub> F <sub>2</sub> , CF <sub>4</sub> , C <sub>2</sub> F <sub>6</sub> , C <sub>3</sub> F <sub>8</sub>
Al-Cu(2%)	BCl <sub>3</sub> /Cl <sub>2</sub> /CHF <sub>3</sub>	Si <sub>3</sub> N <sub>4</sub>	CCl <sub>2</sub> F <sub>2</sub> CHF <sub>3</sub>
Tungsten	SF <sub>6</sub> /Cl <sub>2</sub> /CCl <sub>4</sub>	GaAs	CCl <sub>2</sub> F <sub>2</sub>
TiW	SF <sub>6</sub> /Cl <sub>2</sub> /O <sub>2</sub>		

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# 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.

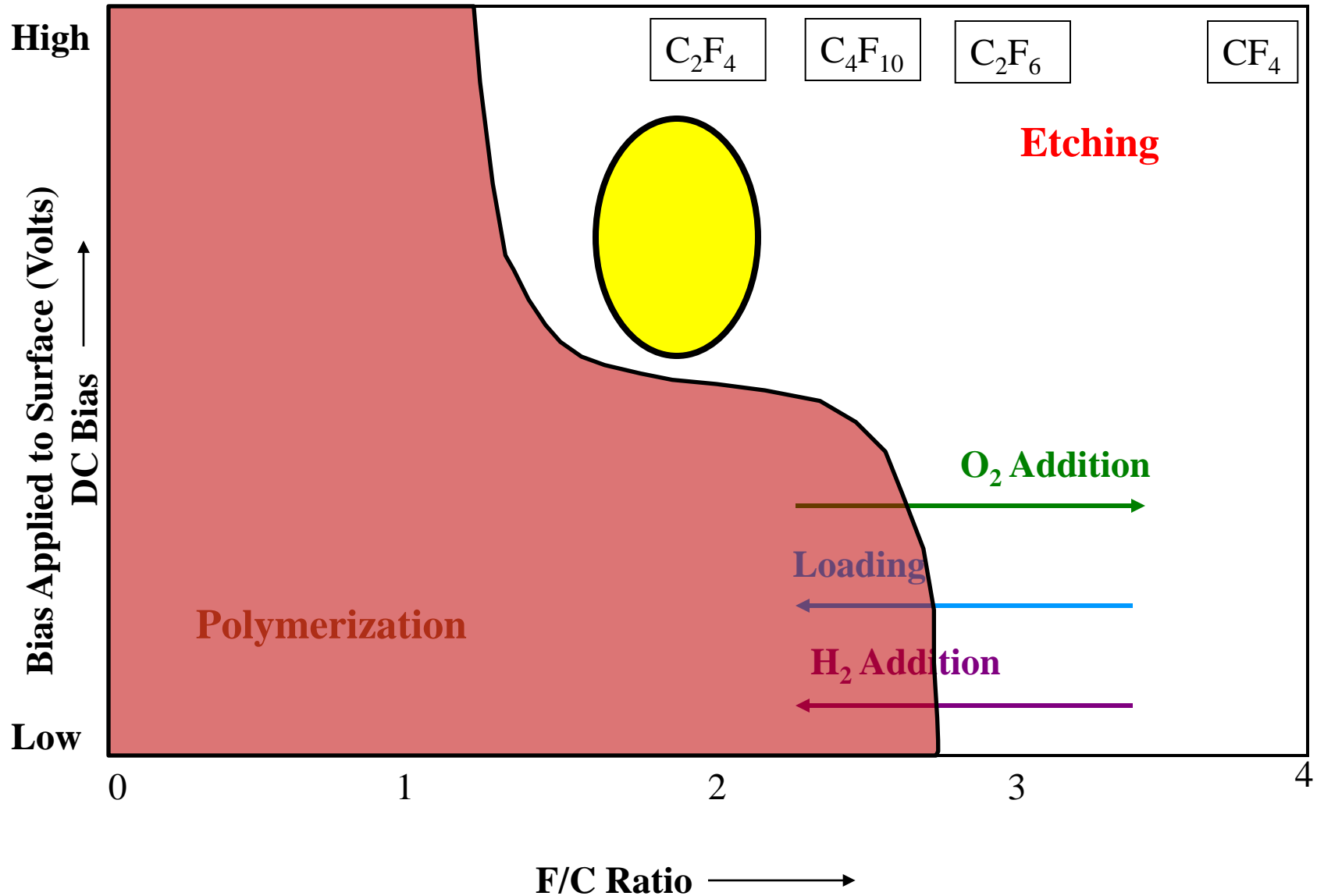
# The “Egg” Chart

- 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  $\text{SiO}_2$
- Naturally this chart is not “exact”, but can be used as a starting point for building a etch recipe.

# Oxide Egg Chart Considerations

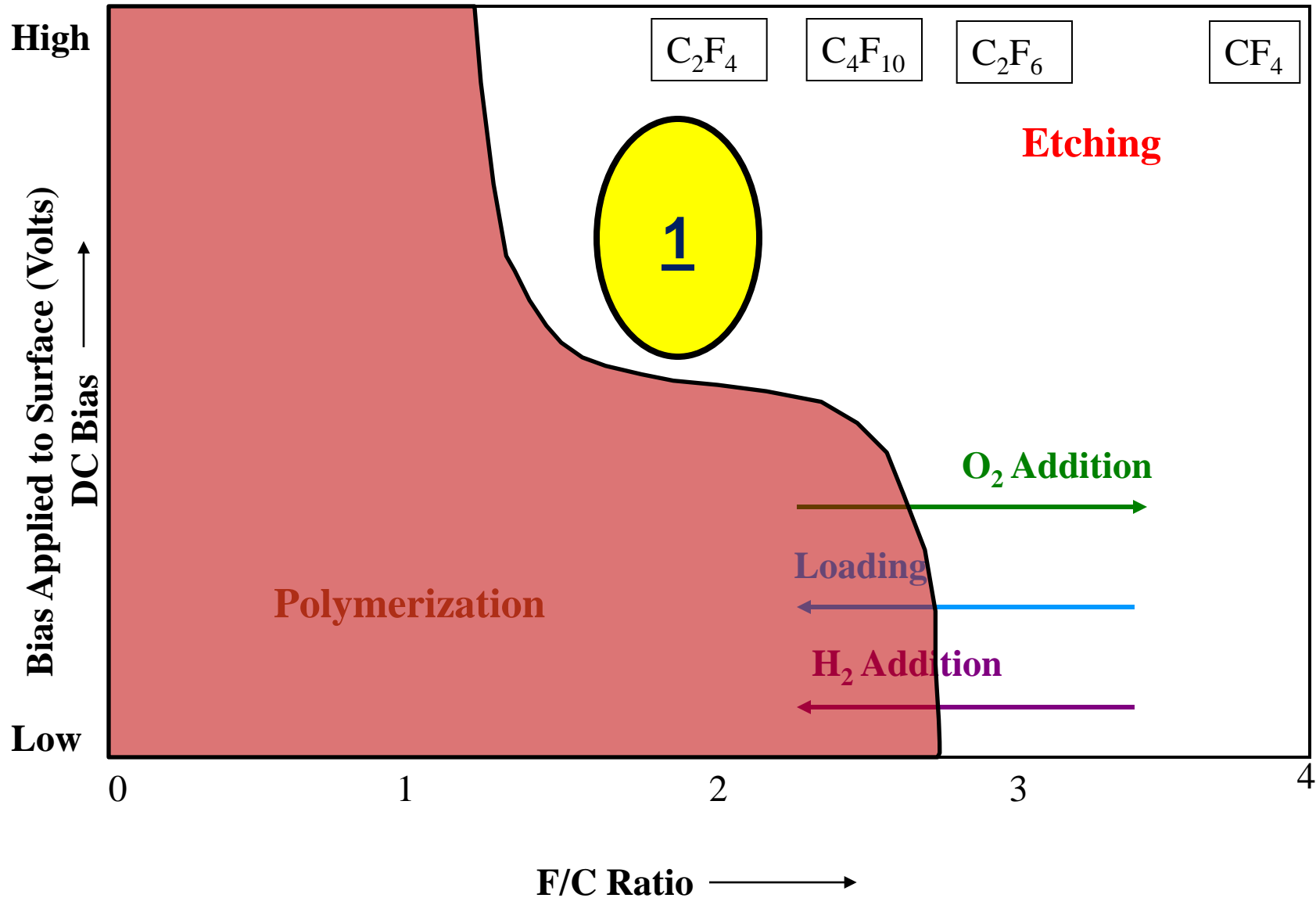
- F/C Ratio- the ratio of fluorine to carbon etching species
- Increasing DC bias, increases bombardment
- The addition of  $H_2$  to the chamber increases polymerization
- The addition of  $O_2$  to the chamber increases free fluorine
- Aspect Ratio- the ratio of depth to width for a small gap, trench,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

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



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



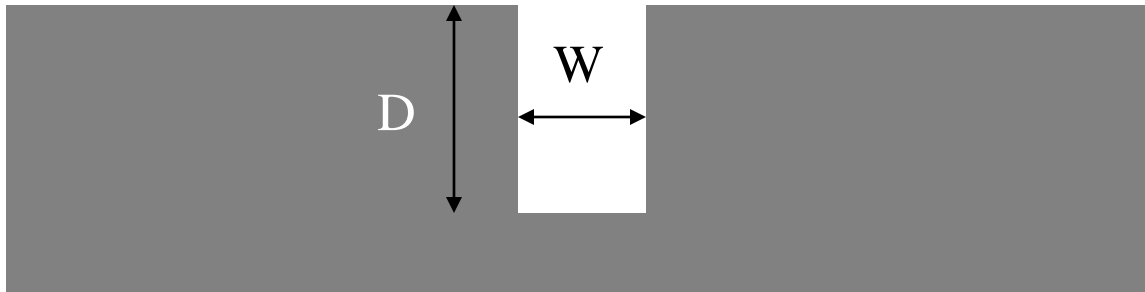
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# The Ideal Profile

- 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

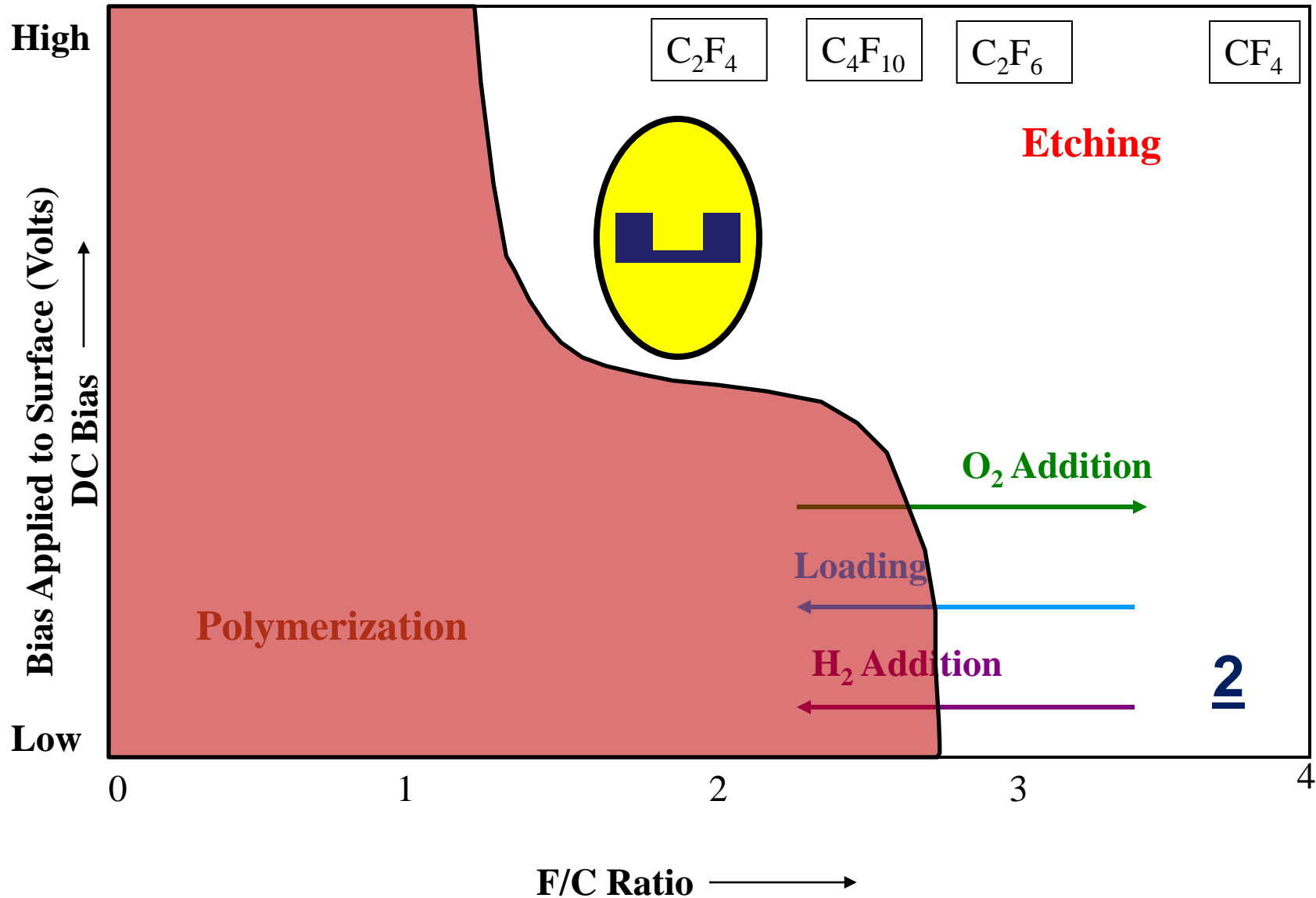


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# Sidewall Profile Two

- 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



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# Sidewall Profile Two

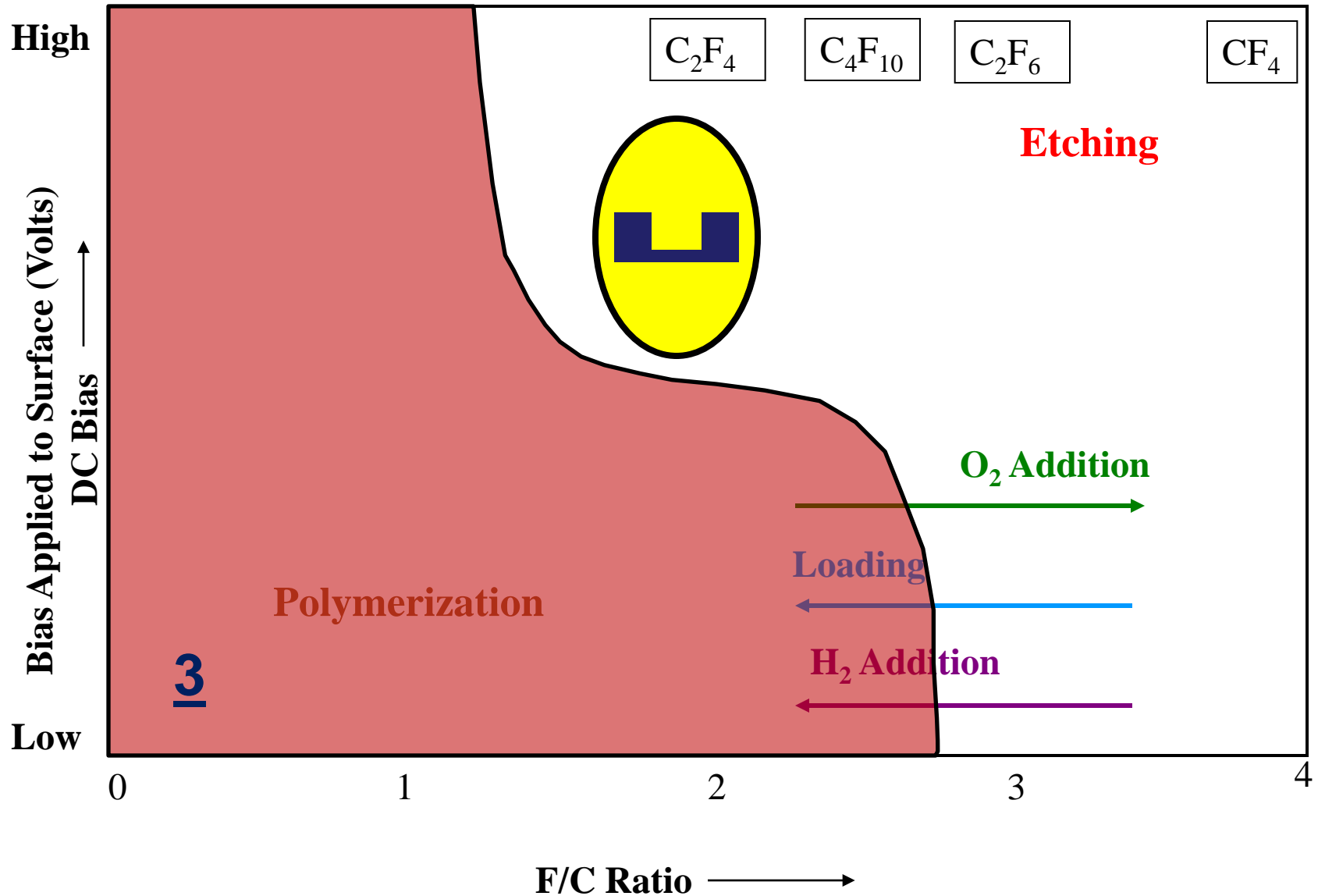


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# Sidewall Profile Three

- 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

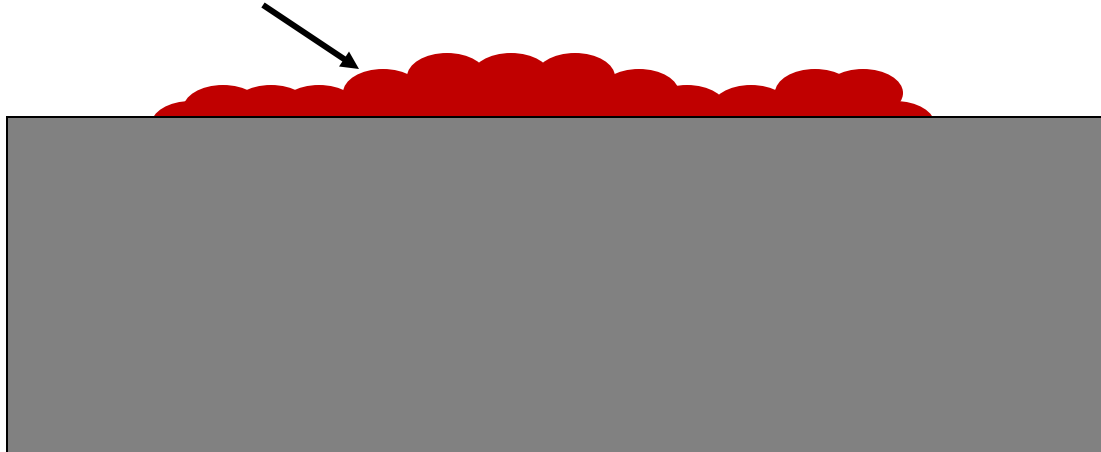
# Fluorine to Carbon Ratio (F/C) of Gas Phase Etching Species vs DC Bias Level



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# Sidewall Profile Three

Polymer buildup



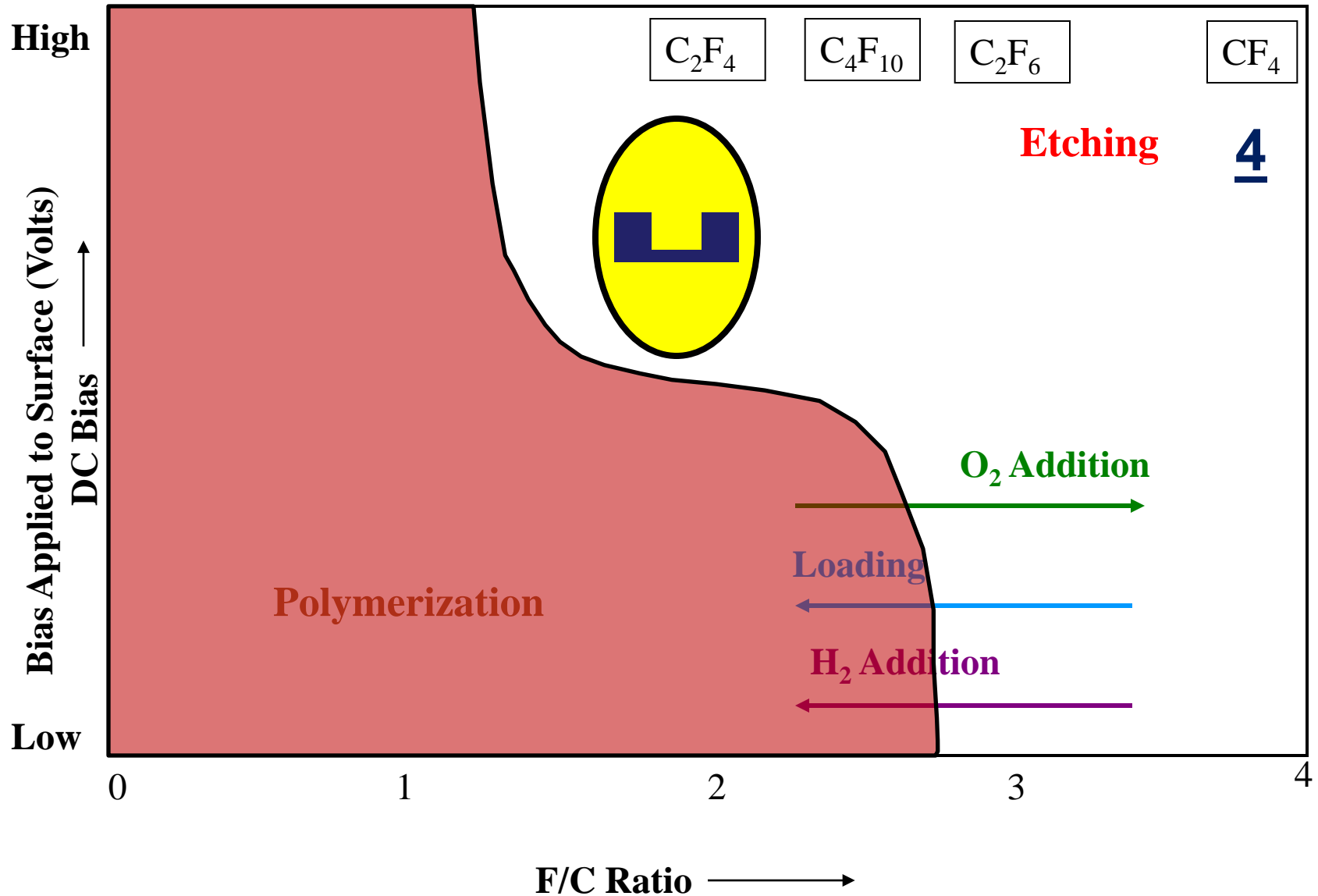
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# Sidewall Profile Four

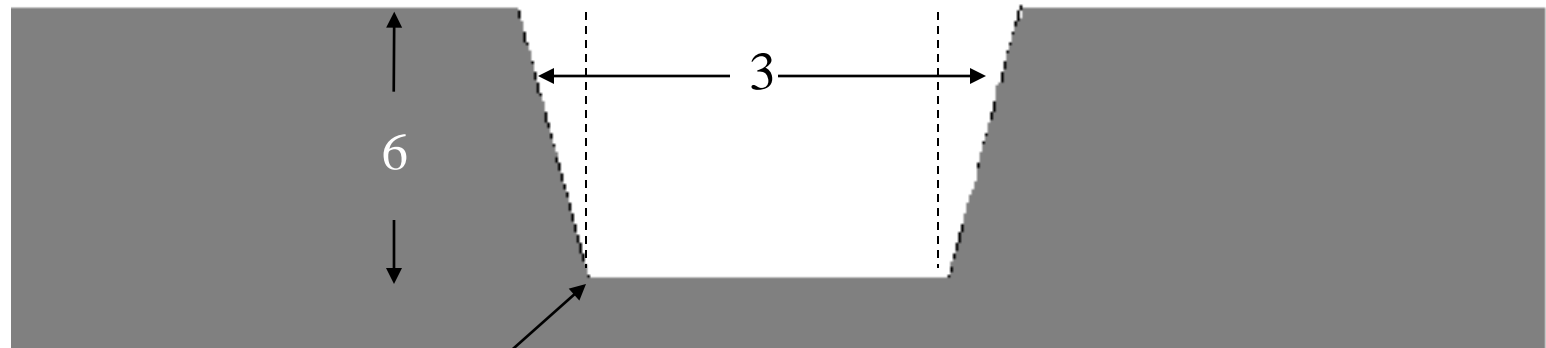
- High DC bias – high bombardment
- No  $H_2$  – no polymerization
- A lot of  $O_2$  – high etch
- F/C ratio = 4,  $SiF_4$  is formed
- Aspect ratio  $>1$ , a dry etch profile

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



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# Sidewall Profile Four



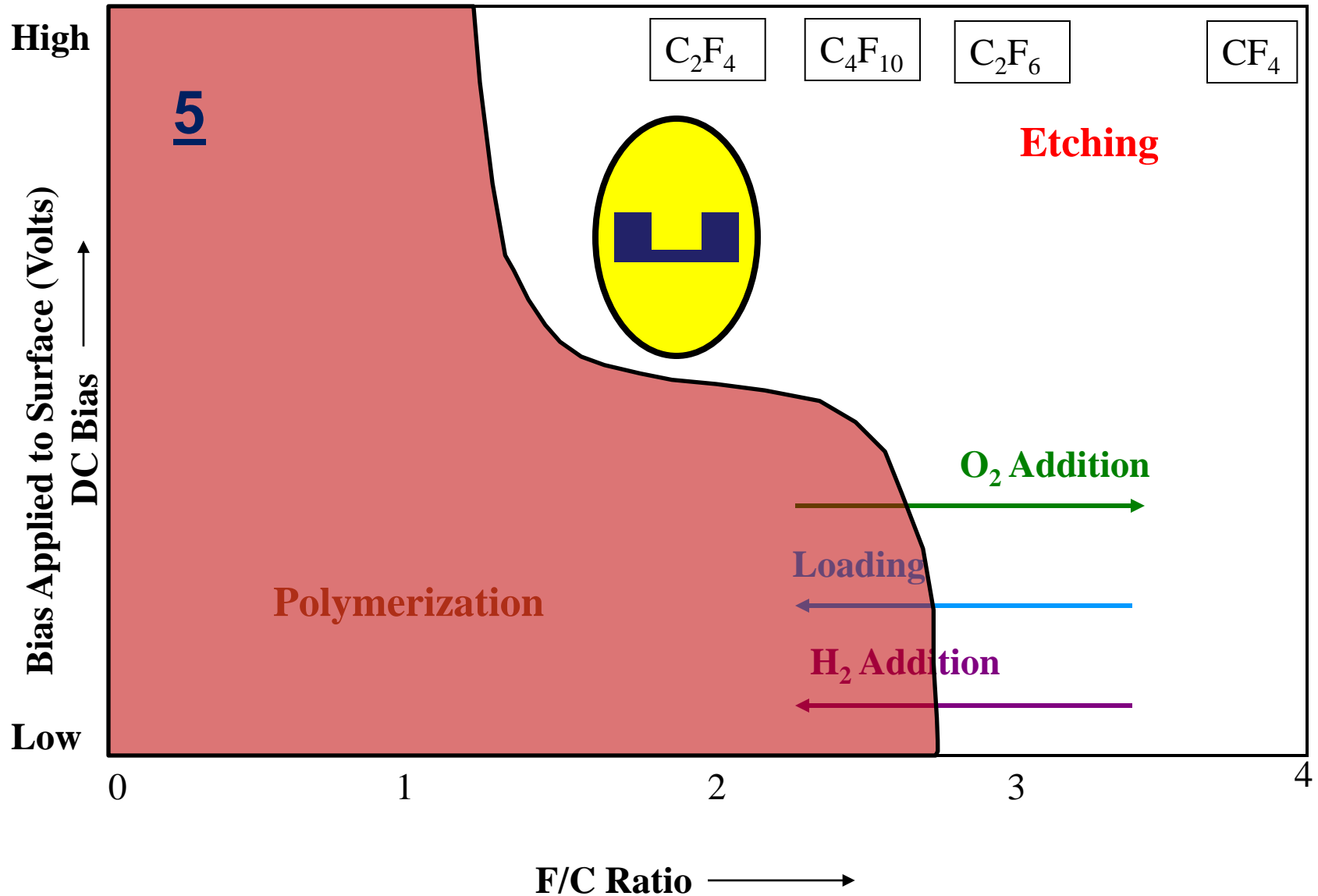
Sharp angles due  
to high bombardment  
with no polymerization

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# Sidewall Profile Five

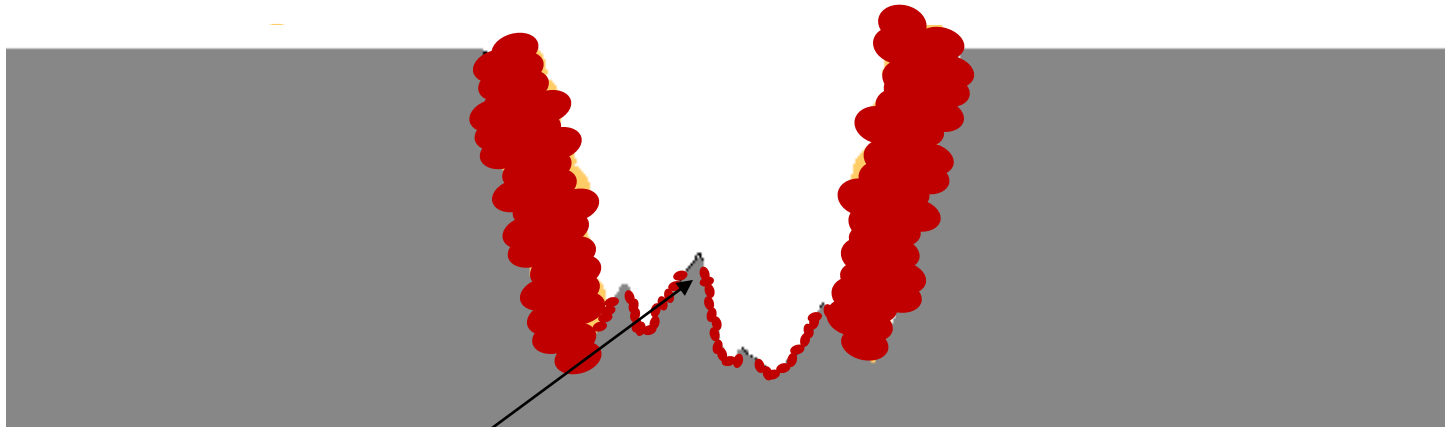
- High DC bias – high bombardment
- A lot of  $H_2$  – a lot of polymerization
- No  $O_2$  – no etch
- F/C ratio =  $1/5$ ,  $SiF_4$  is not formed
- Aspect ratio  $> 1$ , Dry etch profile with undesirable features

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



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# Sidewall Profile Five



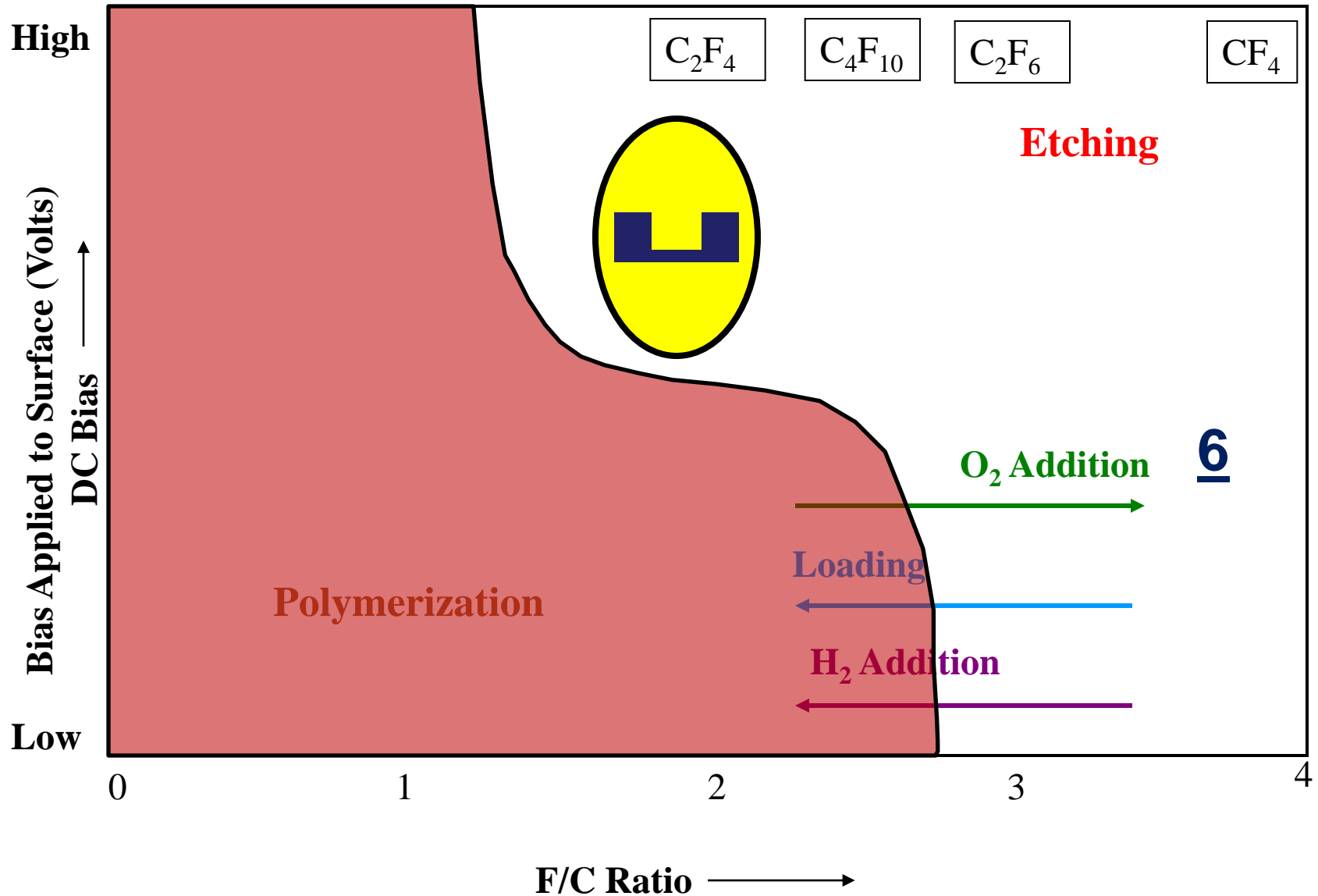
Jagged features  
due to  
polymer buildup

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# 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

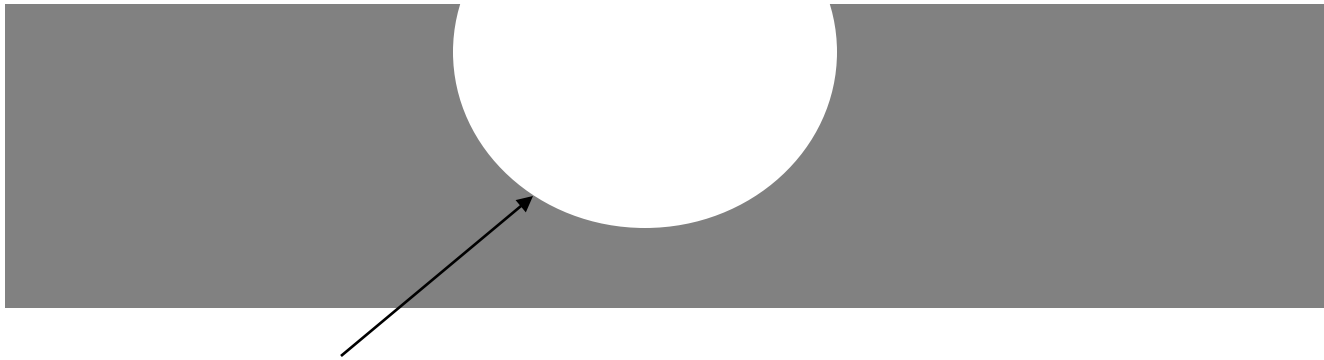
# Fluorine to Carbon Ratio (F/C) of Gas Phase Etching Species vs DC Bias Level



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# Sidewall Profile Six



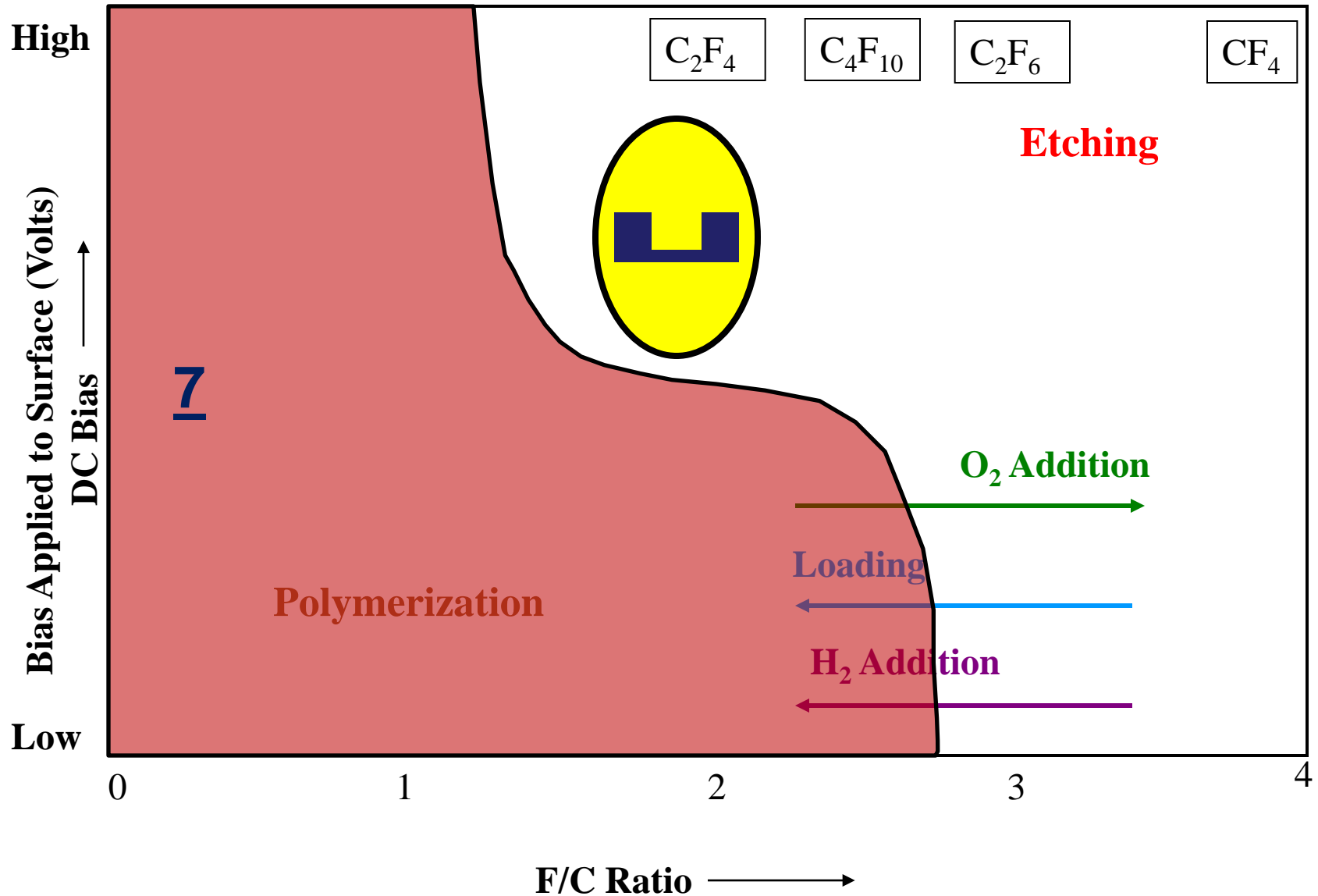
Wider and deeper  
than profile one  
due to increased  
bombardment

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# 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 =  $\frac{1}{4}$ ,  $SiF_4$  is not formed
- Aspect ratio  $> 1$ , Dry etch profile with undesirable features

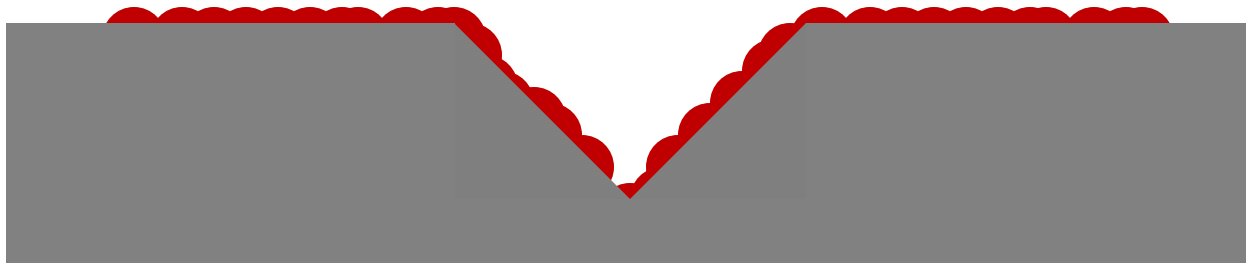
# Fluorine to Carbon Ratio (F/C) of Gas Phase Etching Species vs DC Bias Level



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# Sidewall Profile Seven

Less bombardment than profile four



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# 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

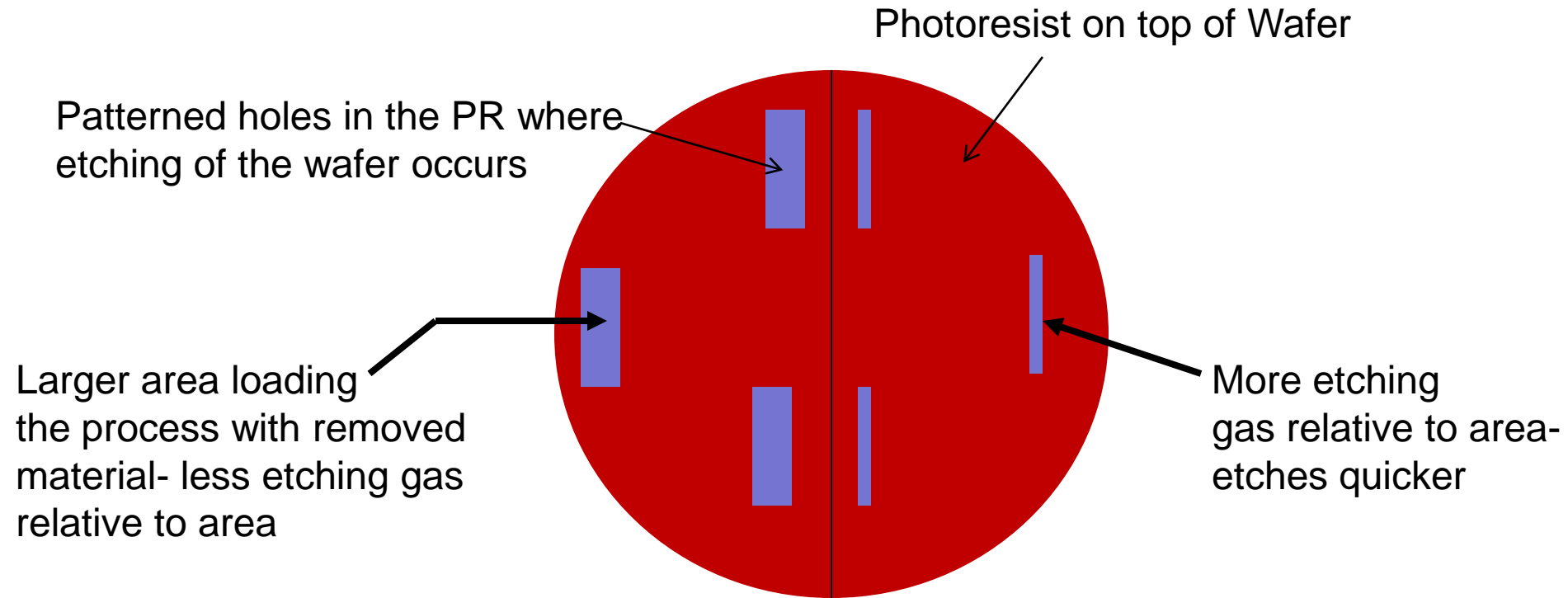
# Residence Time

- 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

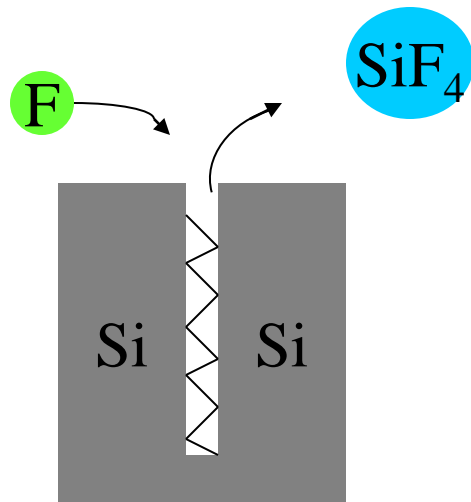
# Microloading



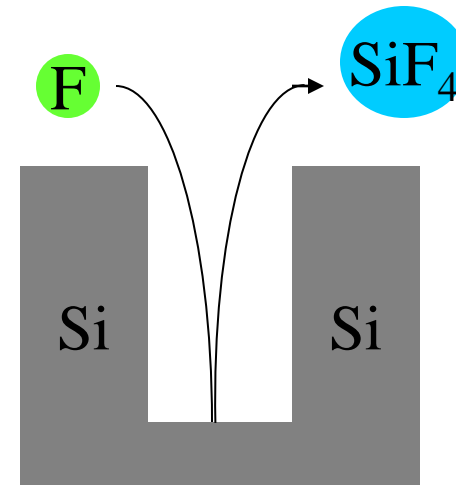
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# Proximity Effect- Etch Rate Based on Feature Size



“Crowded”-  
harder to remove byproducts,  
slower etch rate



Easier to remove byproducts,  
faster etch rate

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# Etch Evaluation

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

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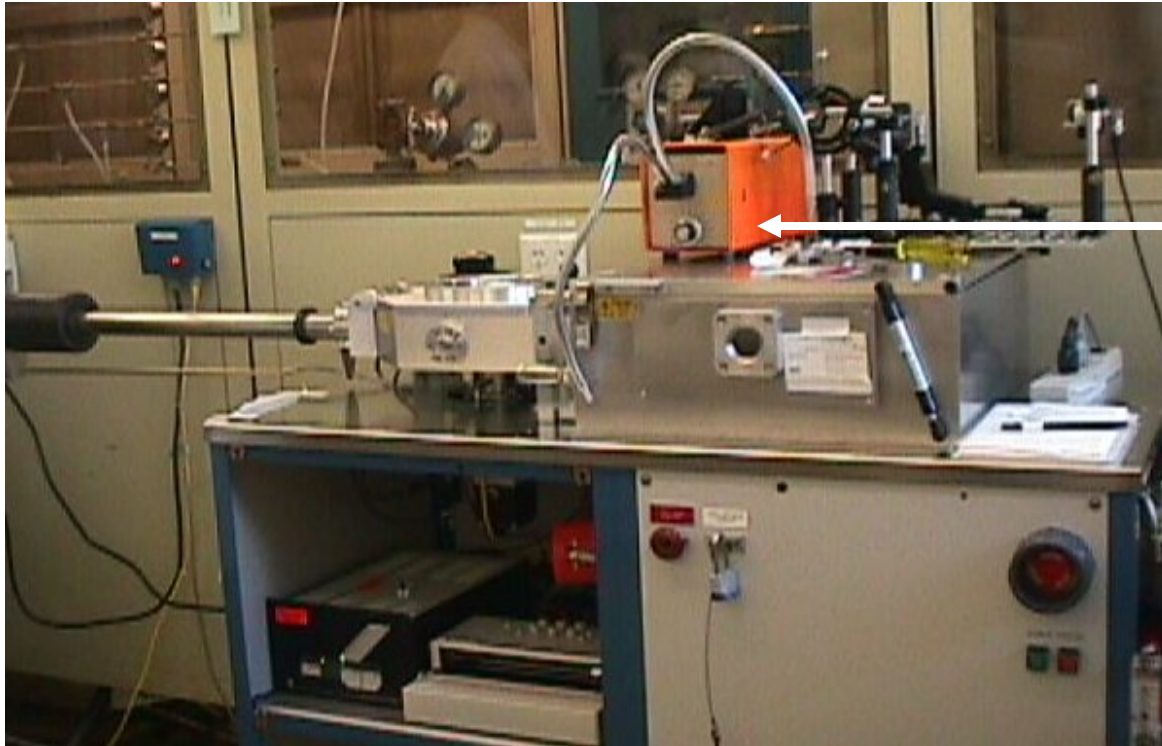
# Endpoint Detection

- 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

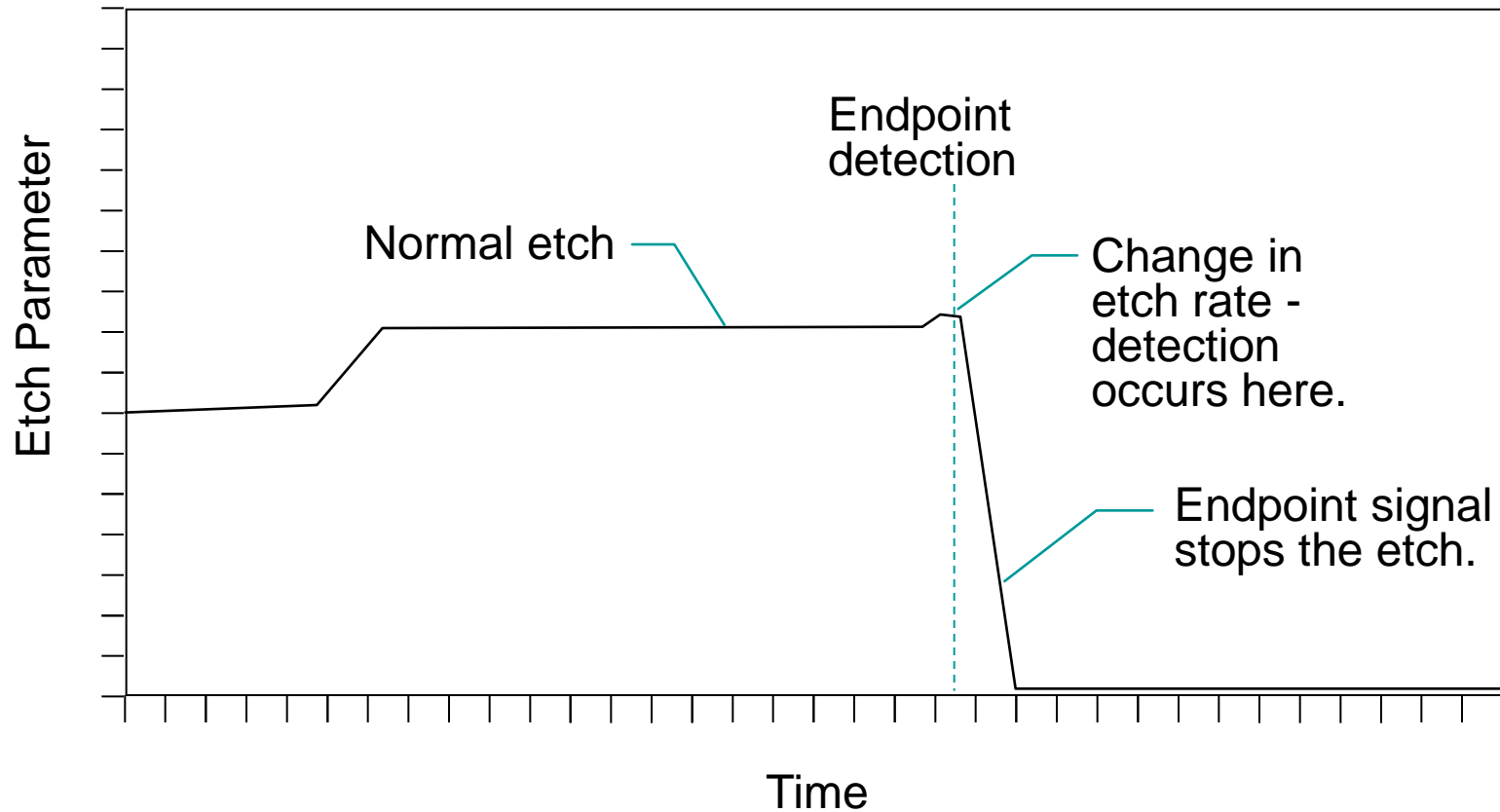
**Oxford Instruments Plasmalab System 100**

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# Optical Emission

Material to be etched	Etchant Gases	Emitting Species	$\lambda(\text{nm})$
Silicon	CF <sub>4</sub> /O <sub>2</sub> ; SF	F(product)	704
	CF <sub>4</sub> /O <sub>2</sub> ; SF	SiF(product)	440, 777
	Cl <sub>2</sub>	SiCl(product)	287
SiO <sub>2</sub>	CHF <sub>3</sub>	CO(product)	484
Si <sub>3</sub> N <sub>4</sub>	CF <sub>4</sub> /O <sub>2</sub>	N <sub>2</sub> (product)	337
	CF <sub>4</sub> /O <sub>2</sub>	CN(product)	387
	CF <sub>4</sub> /O <sub>2</sub>	N(product)	674
	CF <sub>4</sub> /O <sub>2</sub>	F(etchant)	704
Al	Cl <sub>2</sub> ; BCl <sub>3</sub>	Al(product)	391, 394, 396
	Cl <sub>2</sub> ; BCl <sub>3</sub>	AlCl(product)	261
Resist	O <sub>2</sub>	O(etchant)	777, 843
	O <sub>2</sub>	CO(product)	484
	O <sub>2</sub>	OH(product)	309
	O <sub>2</sub>	H(product)	656

# Example Graph of Optical Endpoint Detection



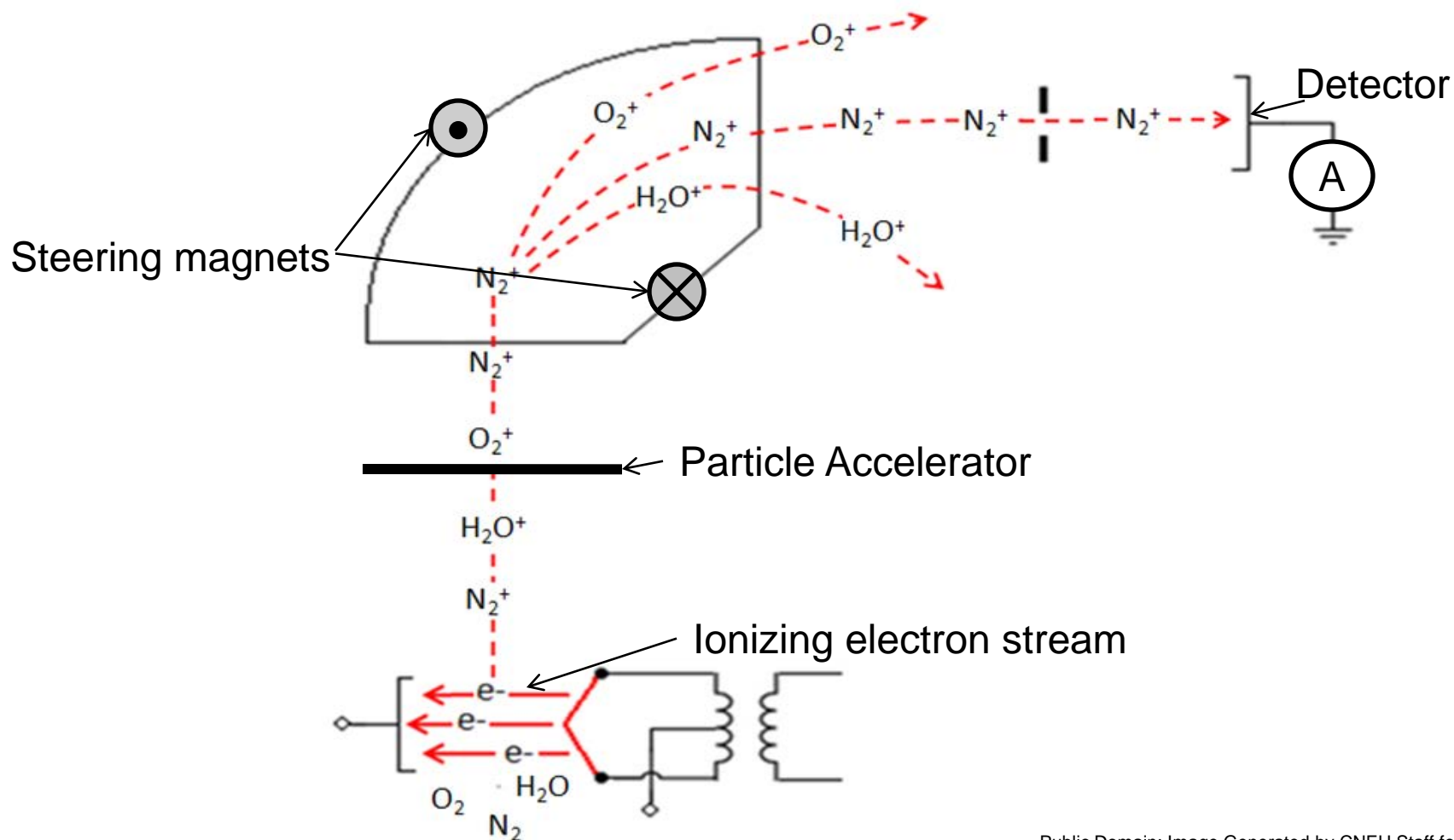
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# Mass Spectroscopy

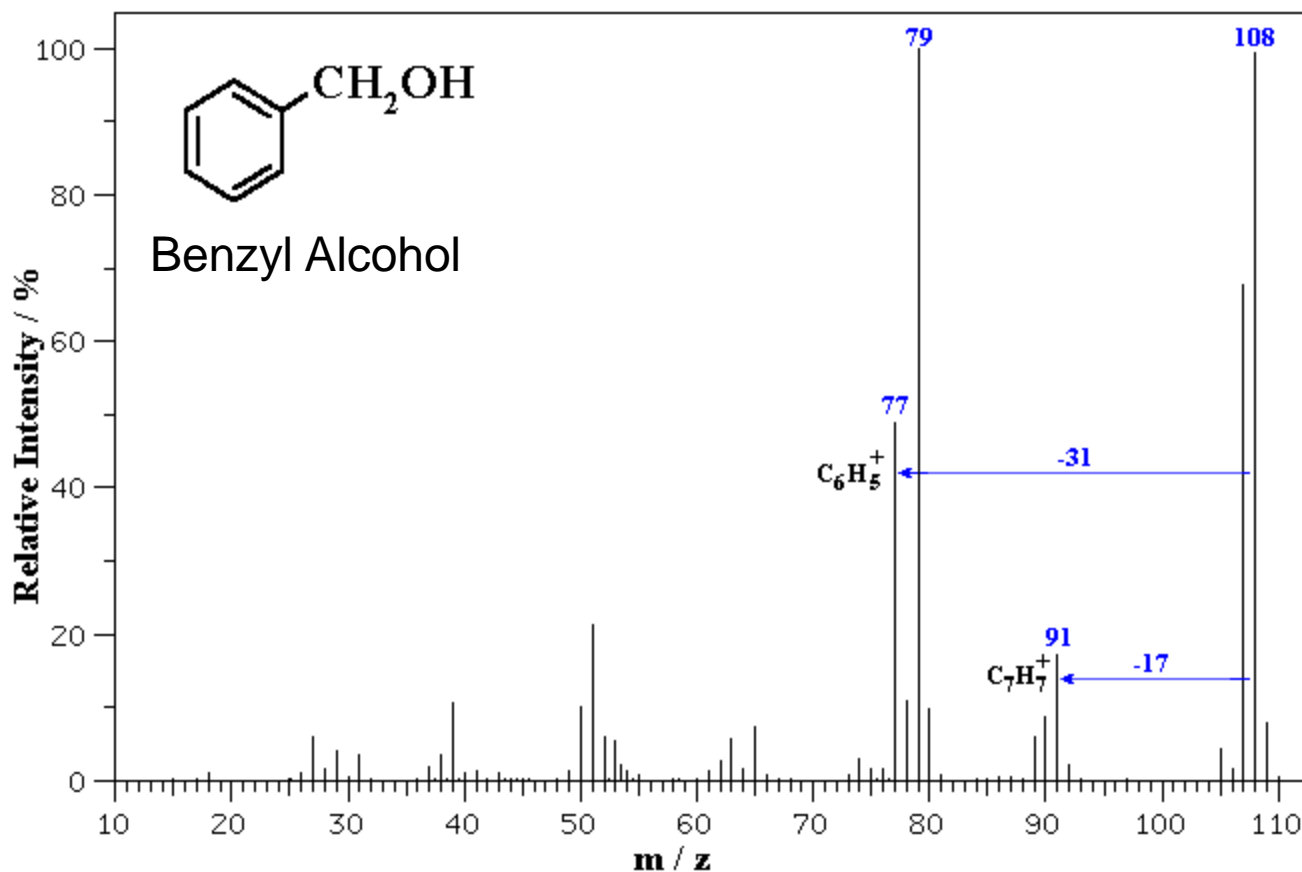
- This method of endpoint detection measures the mass/charge ratio of the etch products
- As the mass/charge ratio peak declines, the products being generated by the etch decline due to the material being etched away
- A residual gas analyzer is a mass spectrometer

# Mass Spectrometer Schematic



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# Example Mass Spectra: Benzyl Alcohol



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