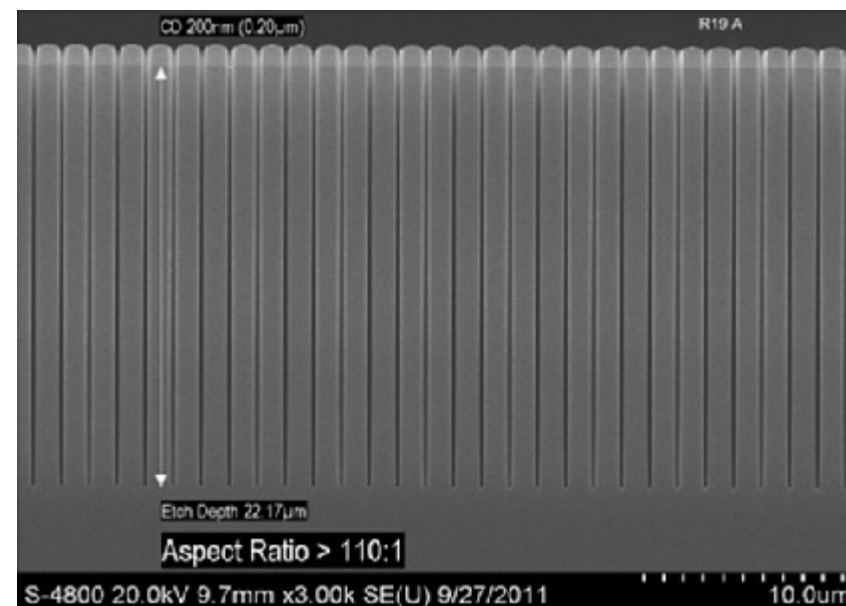
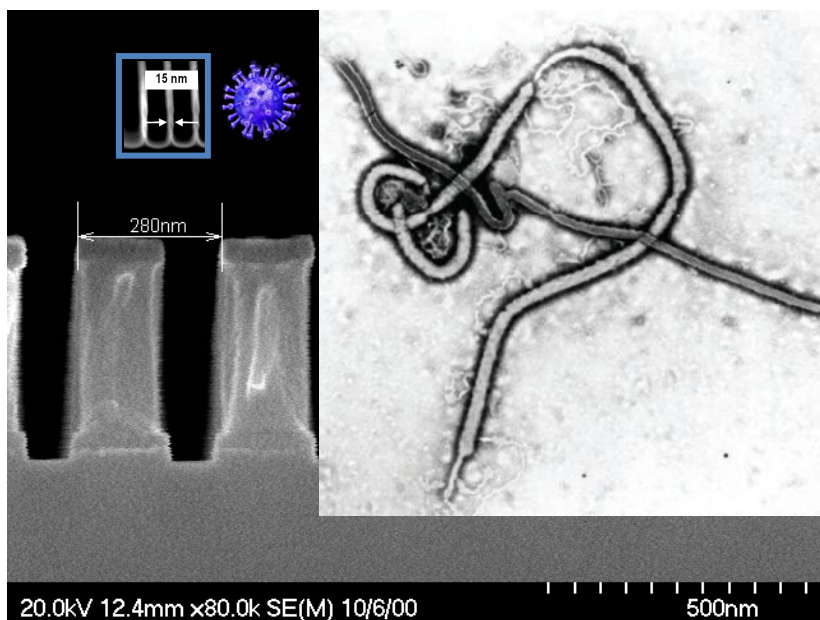


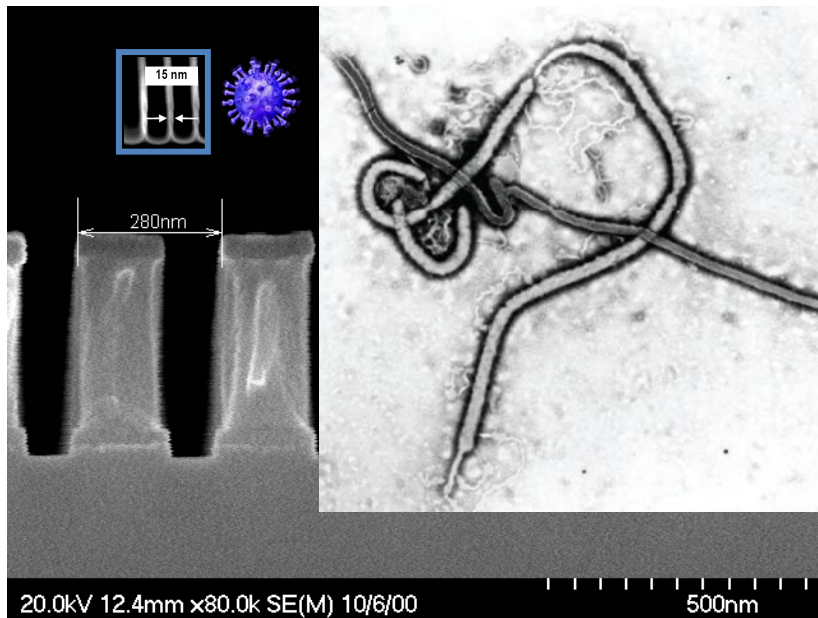
Plasma Science: the unsung engine of the digital age

Steven Shannon
22 June 2022

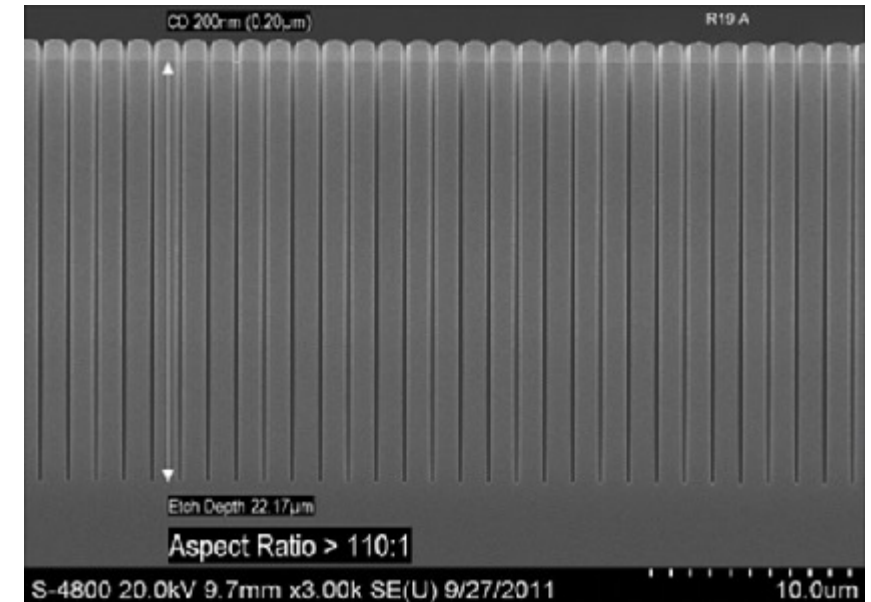


Peter Clarke, "Applied Materials readies DRIE machines for MEMS," *EETimes Magazine*, 22 March 2012

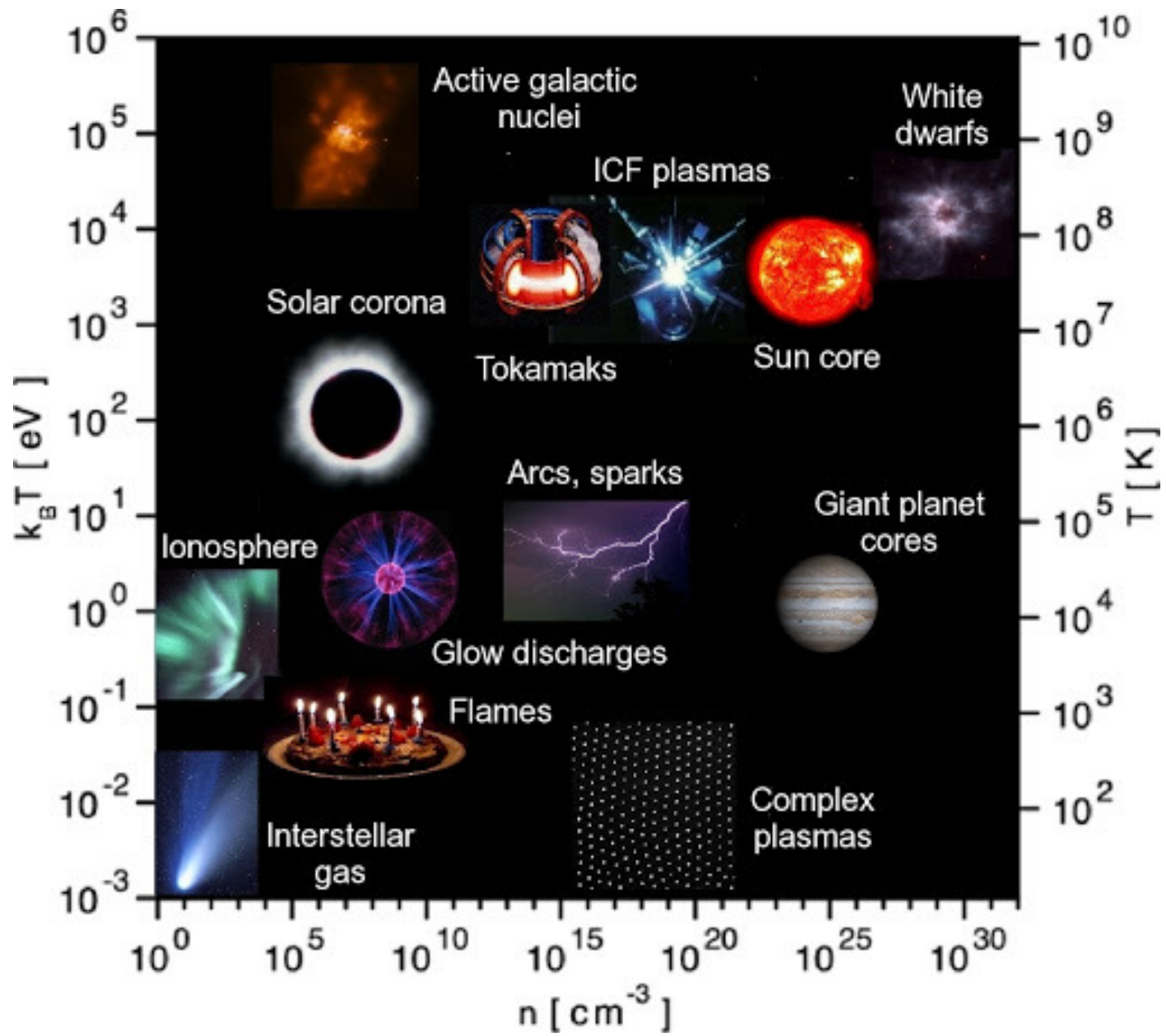
How do we make things so small?
Current SOA is 5nm!!!

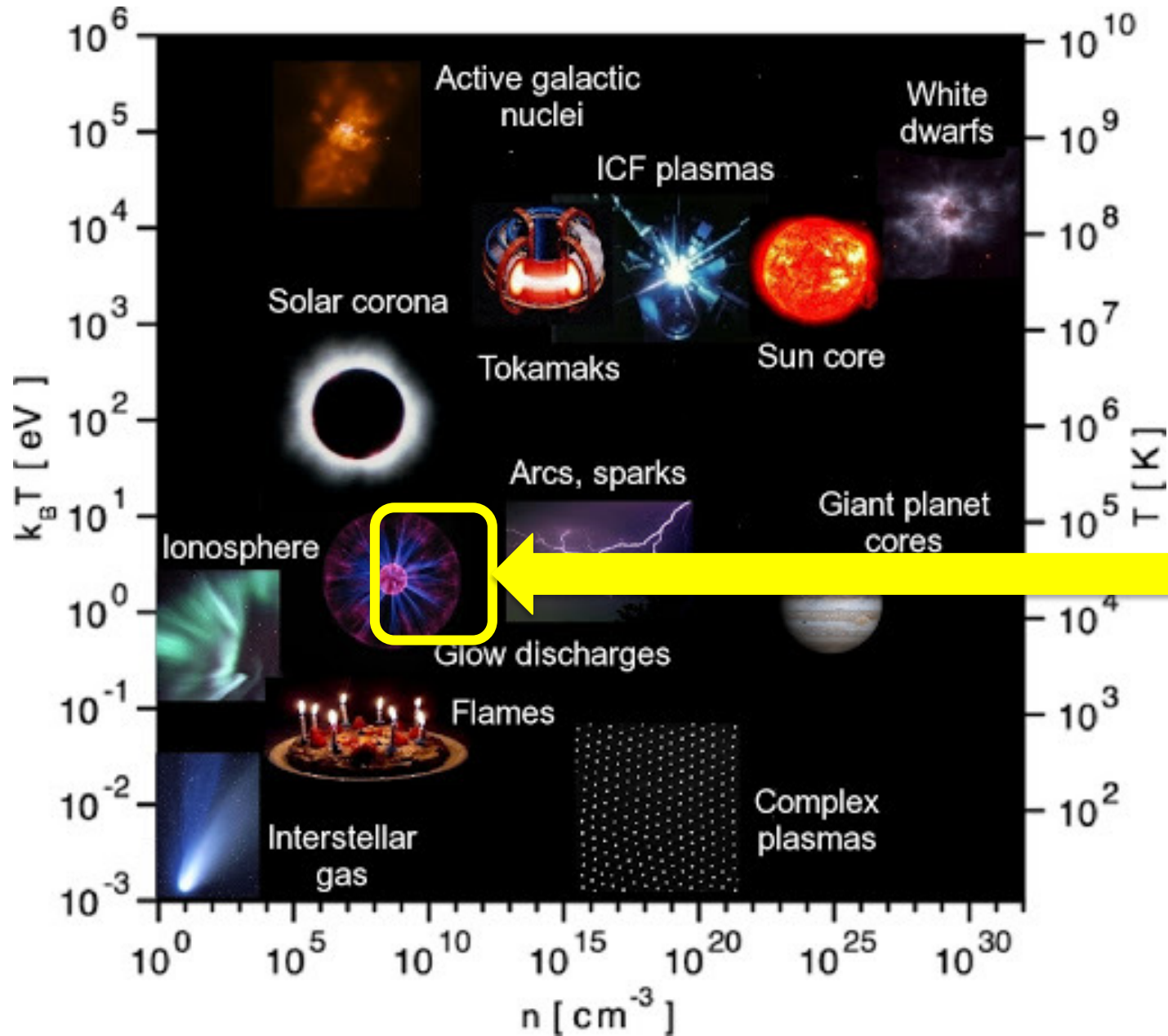


How do we control the direction of a
chemically driven process?



Peter Clarke, "Applied Materials readies DRIE machines for MEMS, *EETimes Magazine*, 22 March 2012





The majority of plasma processing resides in a pretty small window in “plasma space”

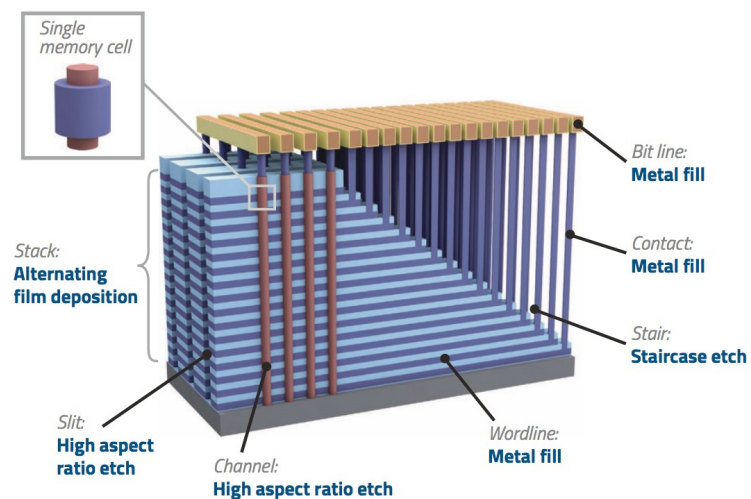
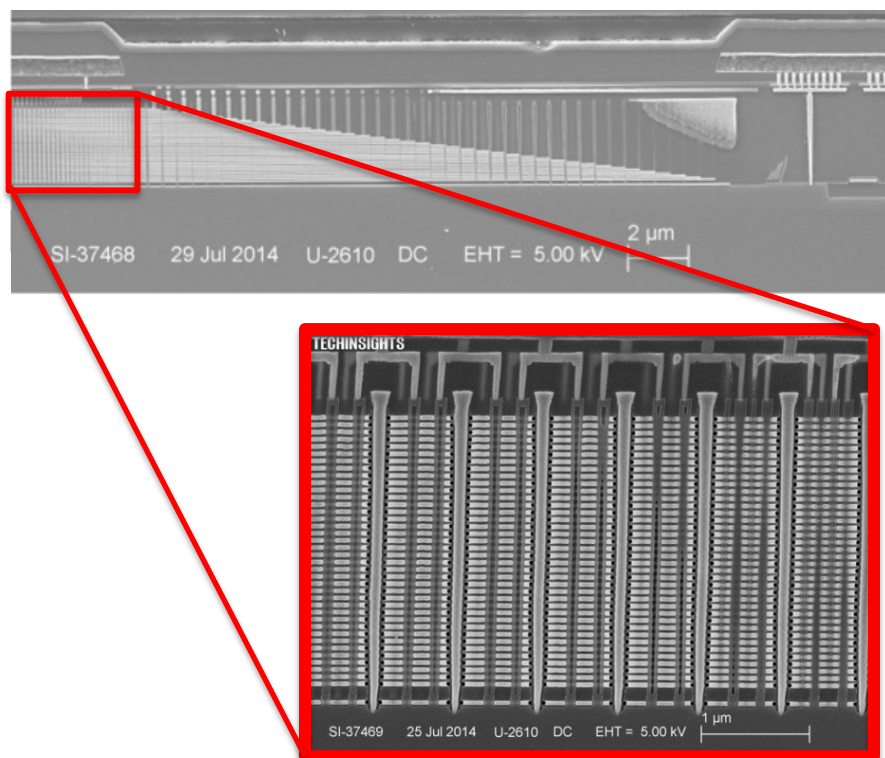
$$10^8 \text{ cm}^{-3} < n_e < 10^{12} \text{ cm}^{-3}$$

$$0.5 \text{ eV} < T_e < 10 \text{ eV}$$

Less than 1% of the gas is actually ionized

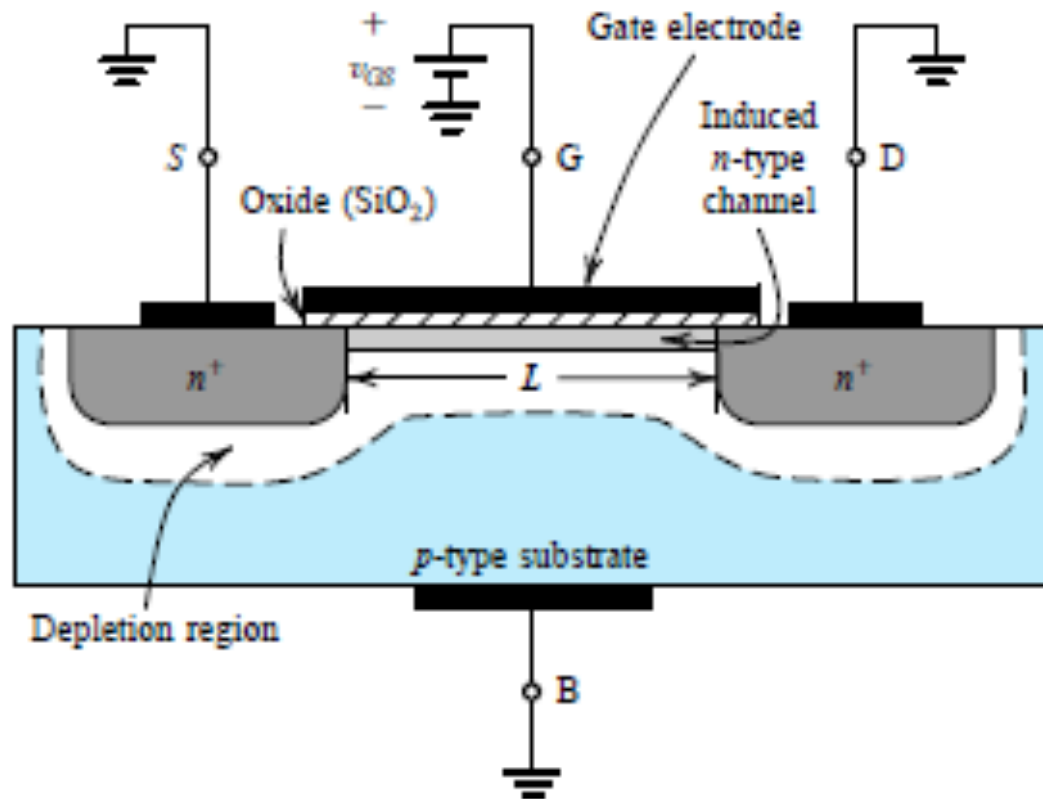
The background gas (and ions) stay roughly near room temperature

The basic challenge – fabrication of very complex features with dimensions ~10nm

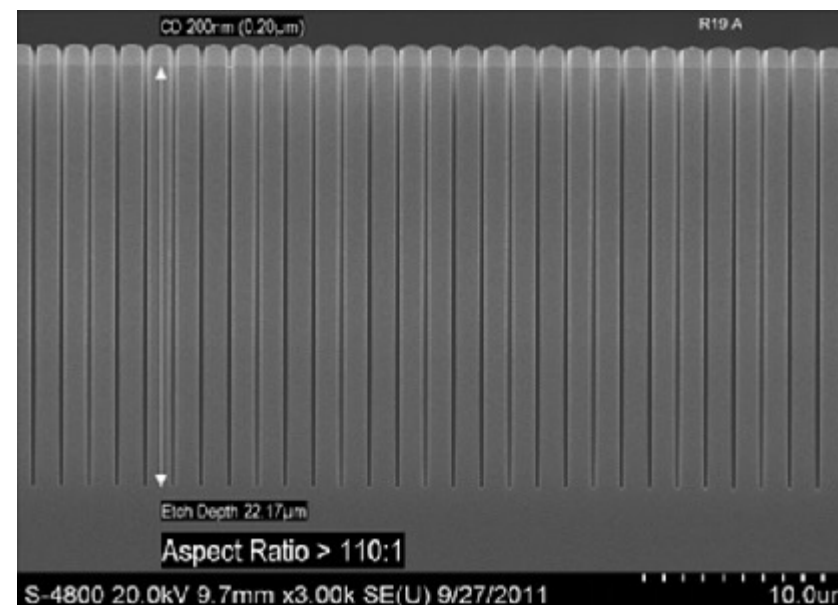
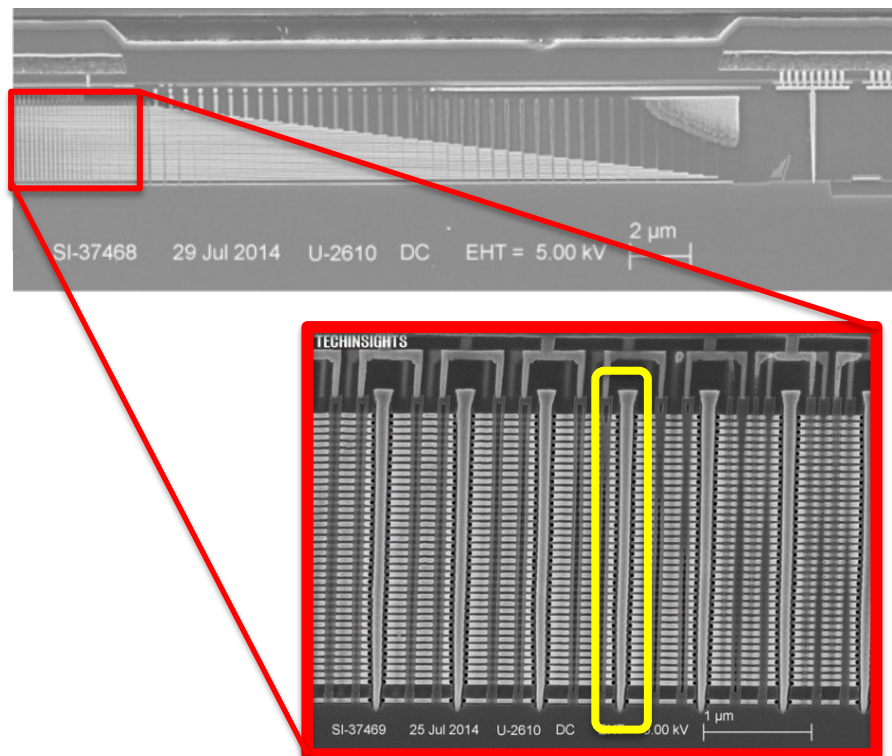


Harmeet Singh, "Overcoming challenges in 3D NAND volume manufacturing, *Solid State Technology Magazine*, July 2017
 Dick James, "The Second Shoe Drops – Samsung V-NAND Flash", www.chipworks.com, 5 August 2014

Why? Because the smaller the device, the faster it runs...

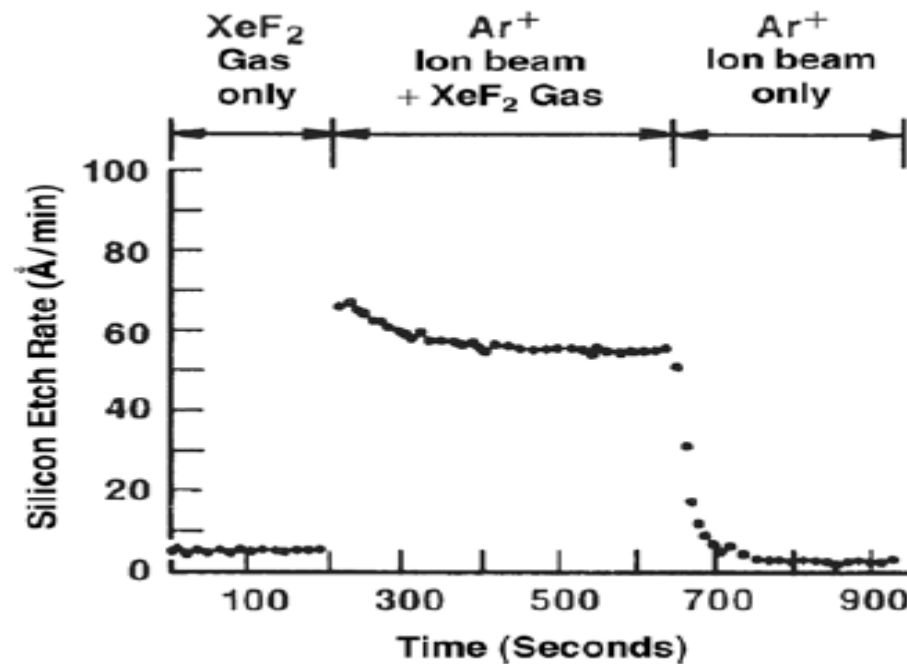
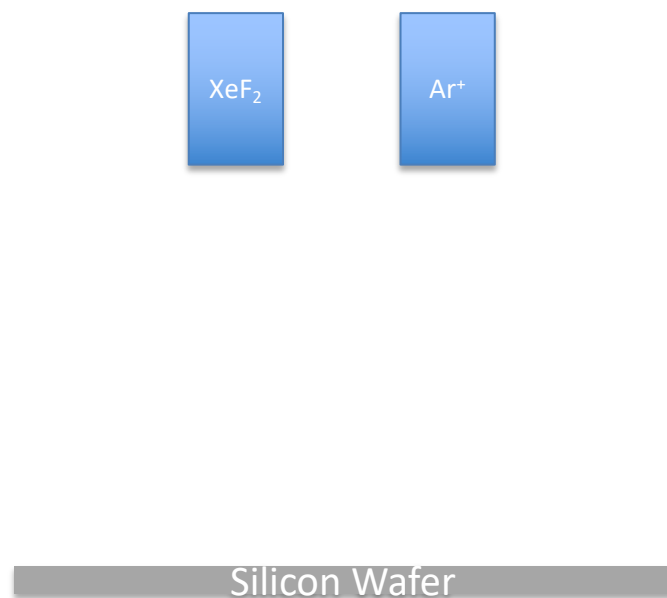


There are lots of challenges to make this device... we will focus on High Aspect Ratio etching in dielectric materials



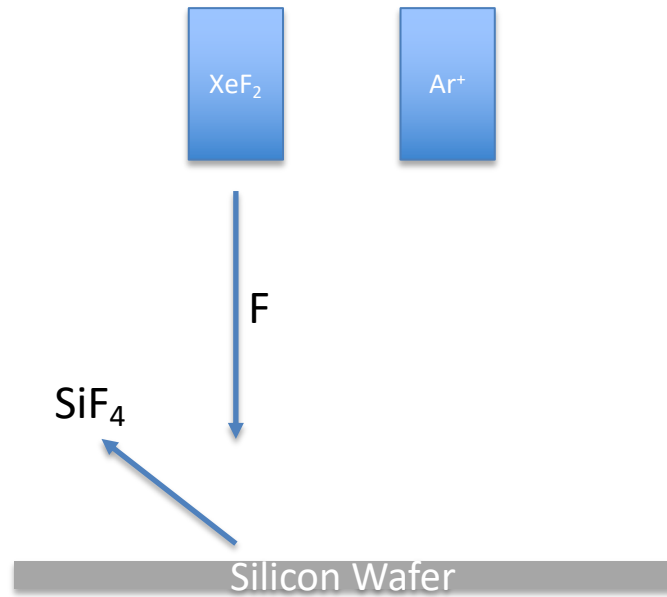
Peter Clarke, "Applied Materials readies DRIE machines for MEMS, *EETimes Magazine*, 22 March 2012

The “classic” experiment that drove plasma etch

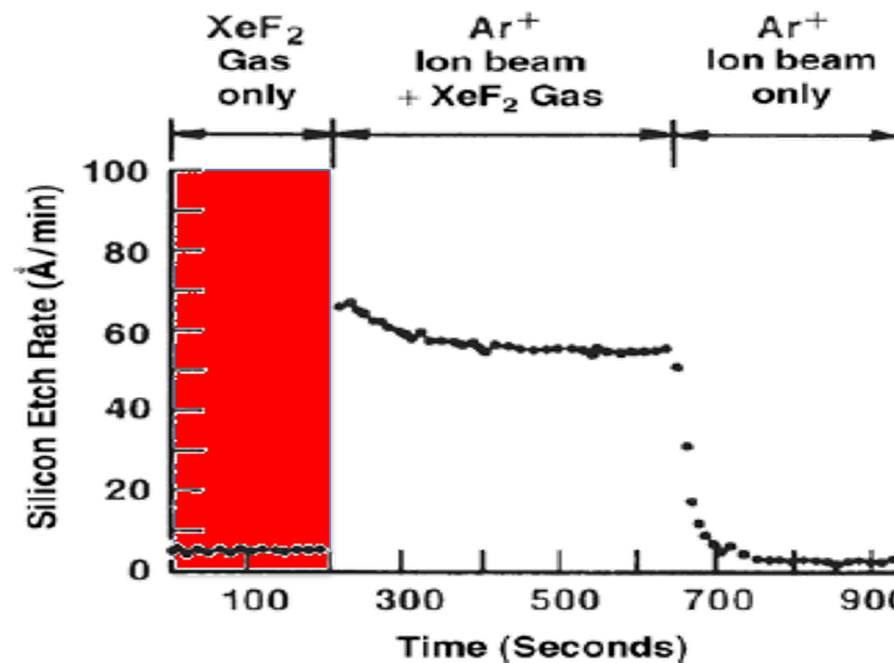
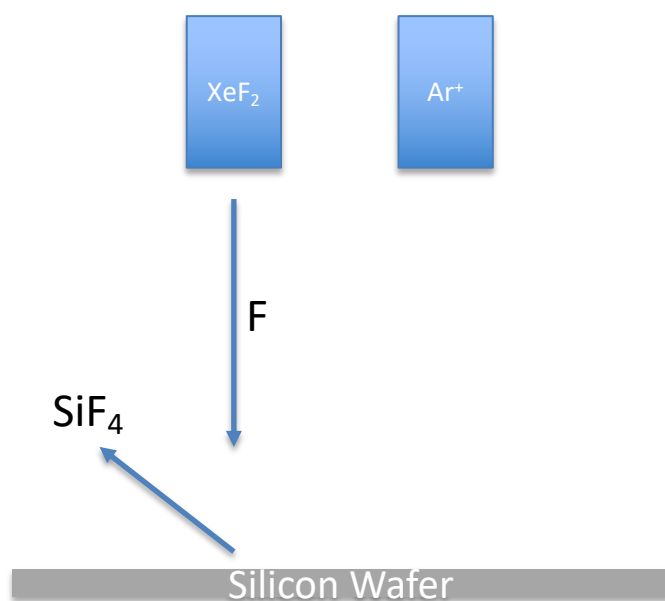


Coburn and Winters, J. Vac. Sci. Technol. **16**, 391

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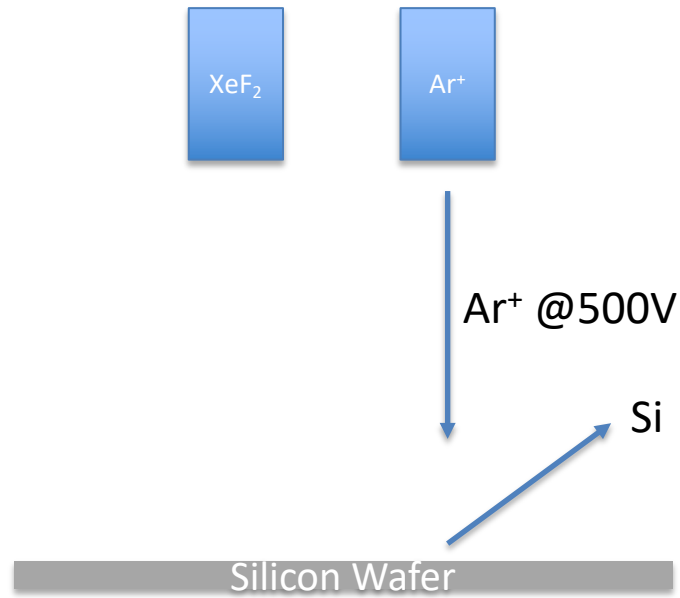


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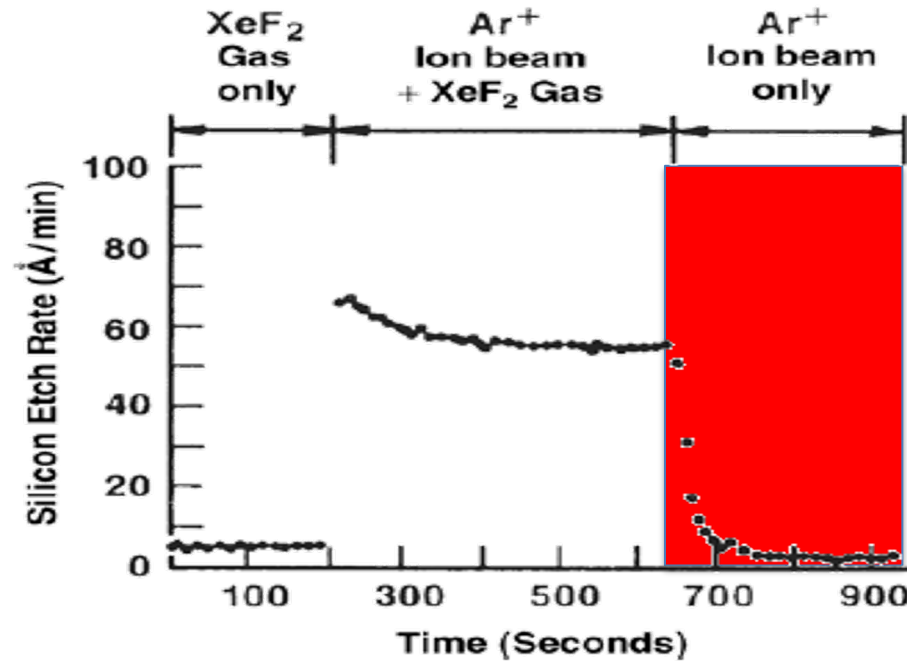
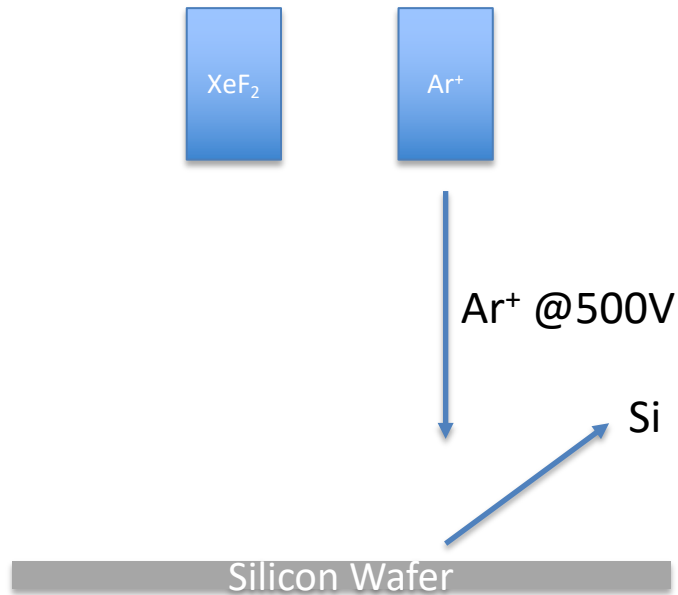


Coburn and Winters, J. Vac. Sci. Technol. **16**, 391

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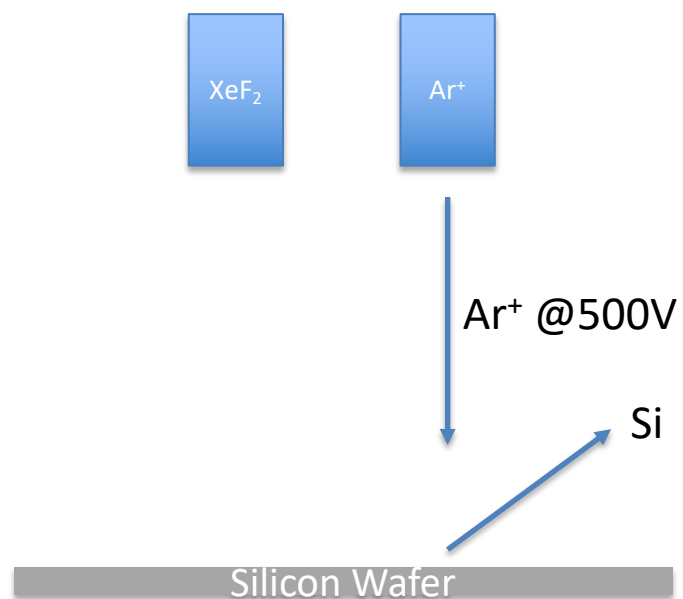


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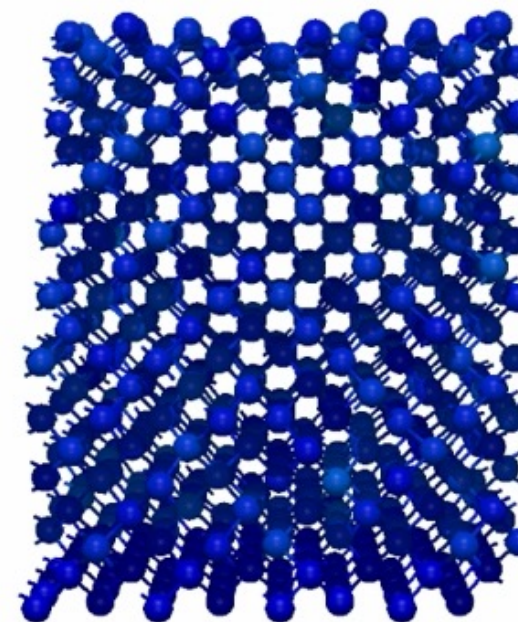


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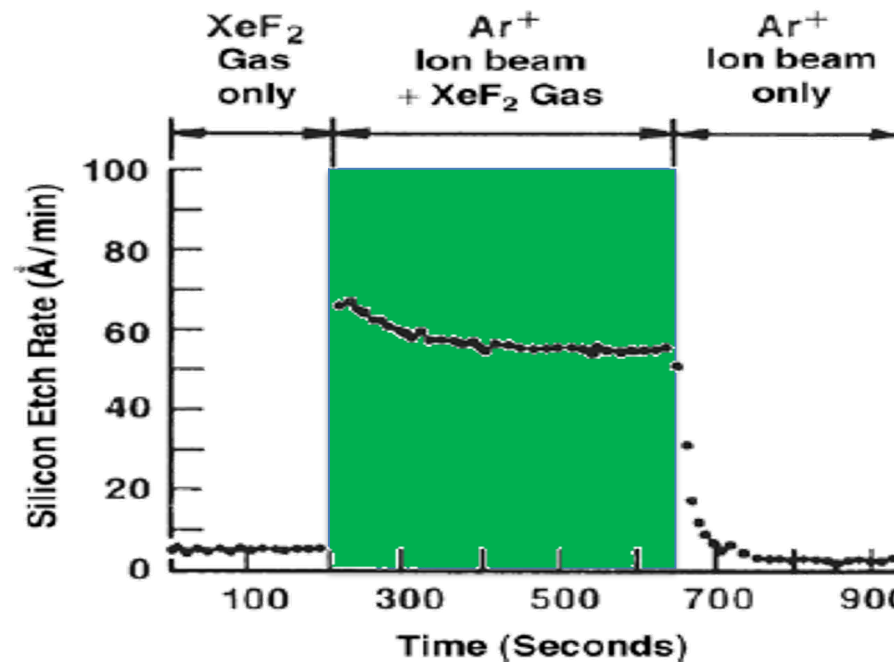
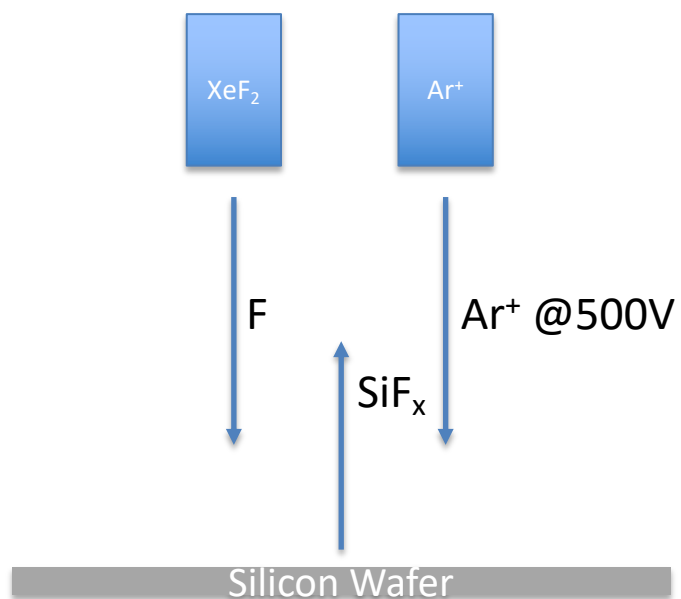


Initially Crystalline Si at 300 K



MD simulation by Graves group, UC Berkeley

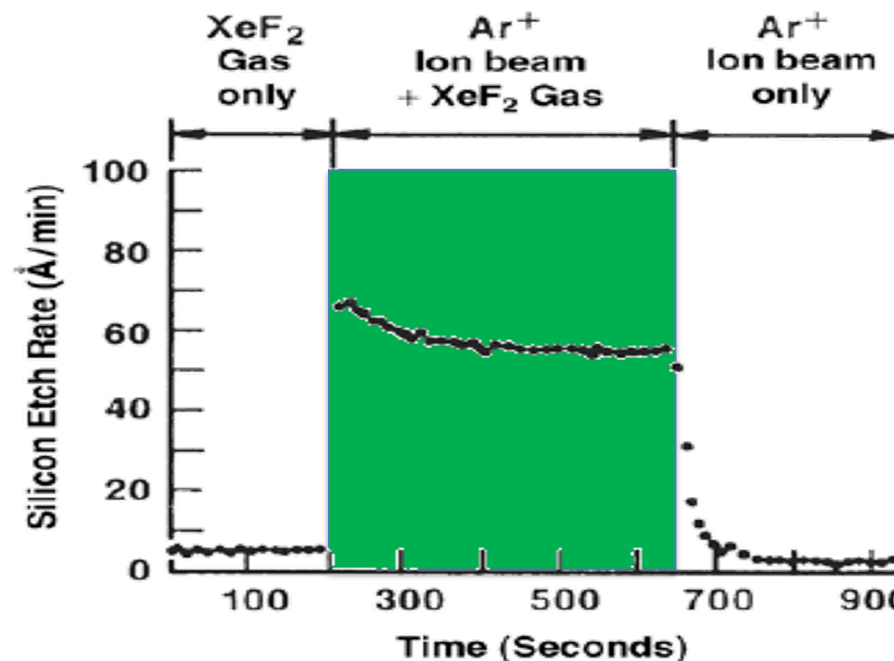
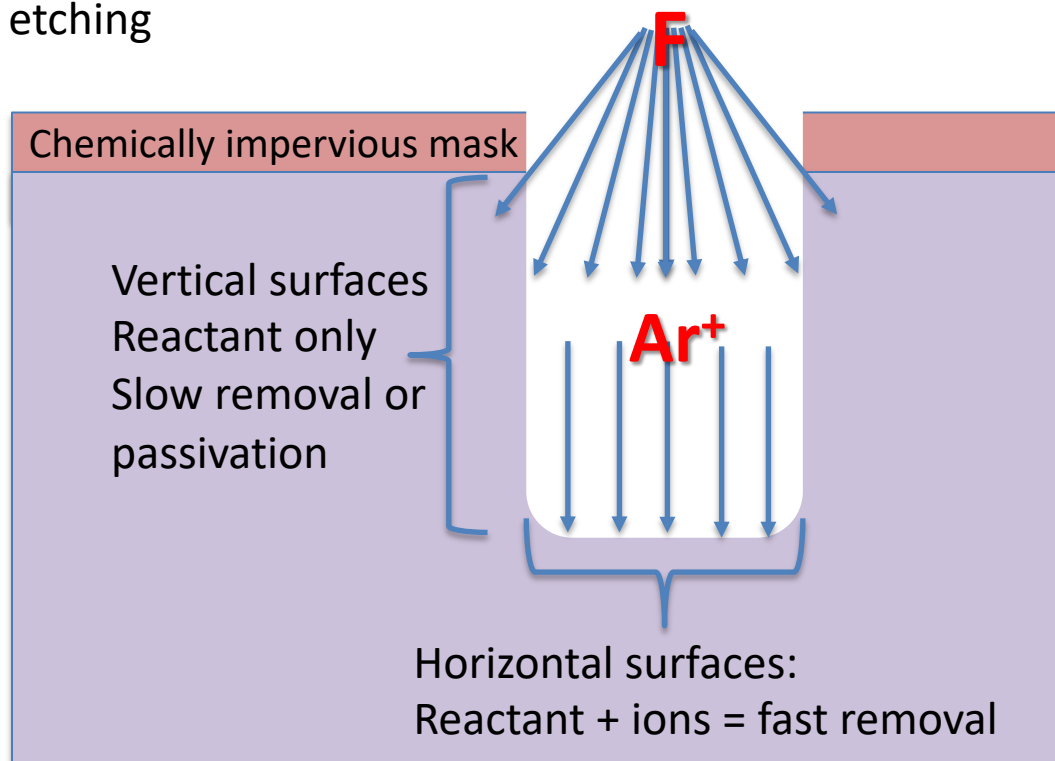
The “classic” experiment that drove plasma etch



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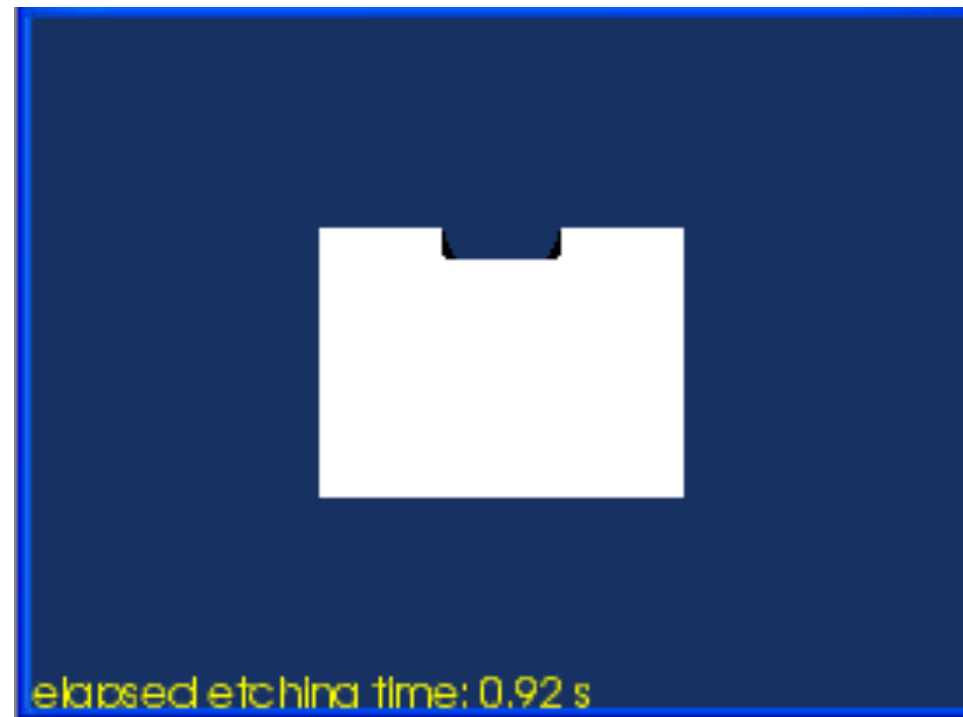
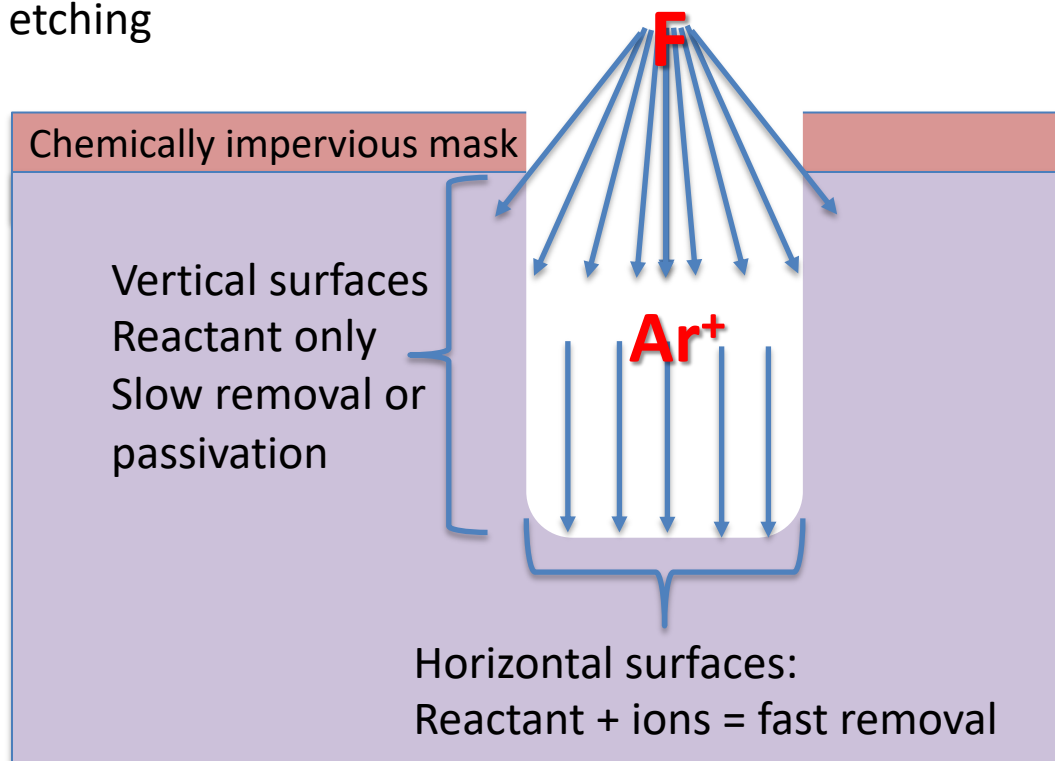
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Coburn and Winters, J. Vac. Sci. Technol. **16**, 391

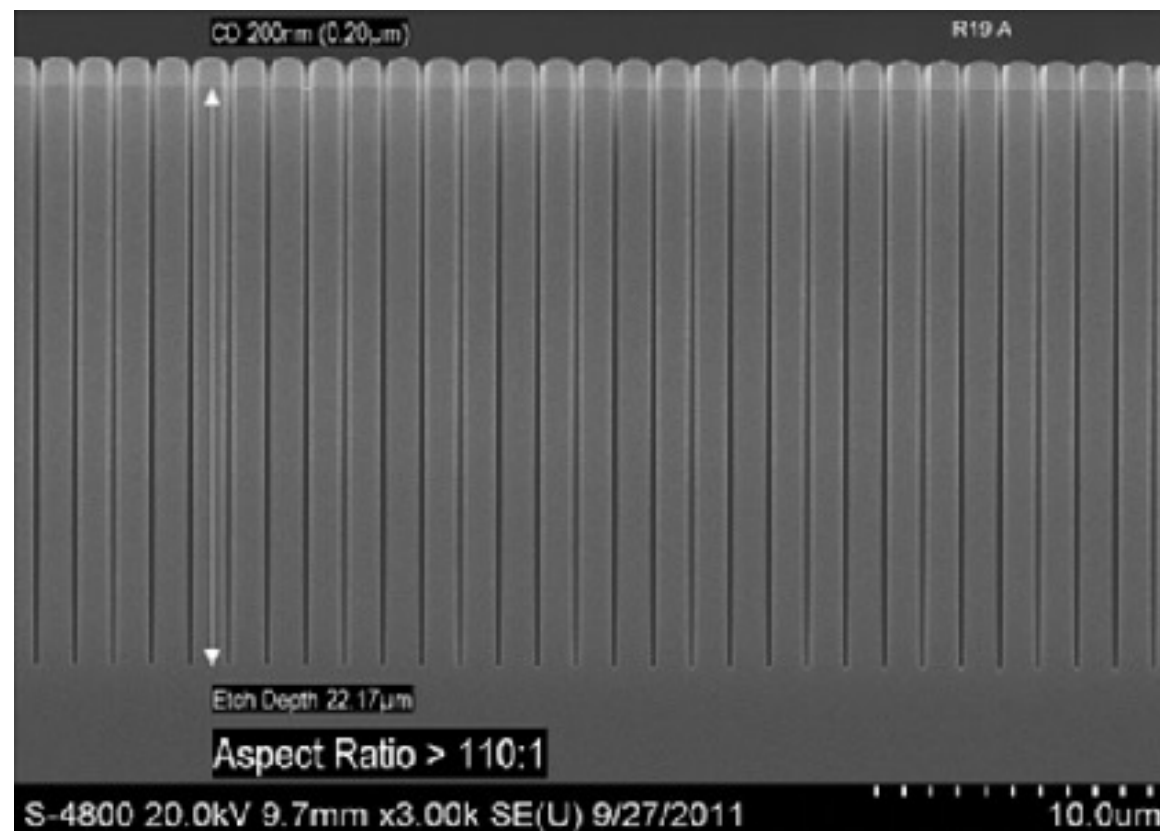
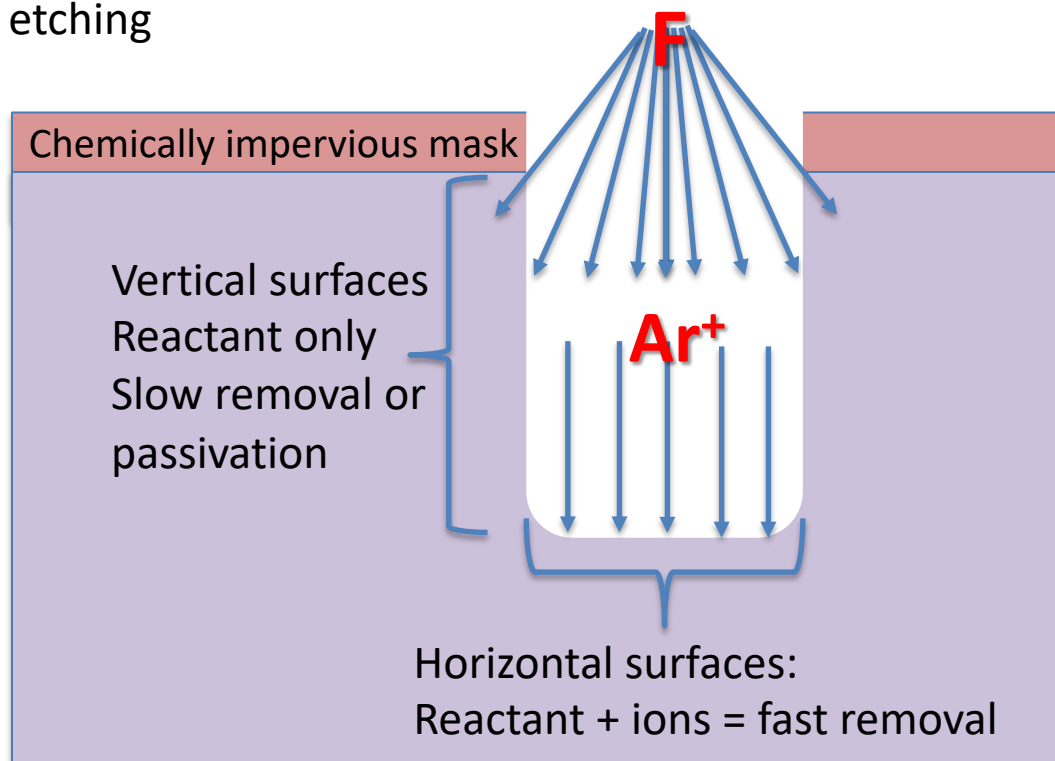
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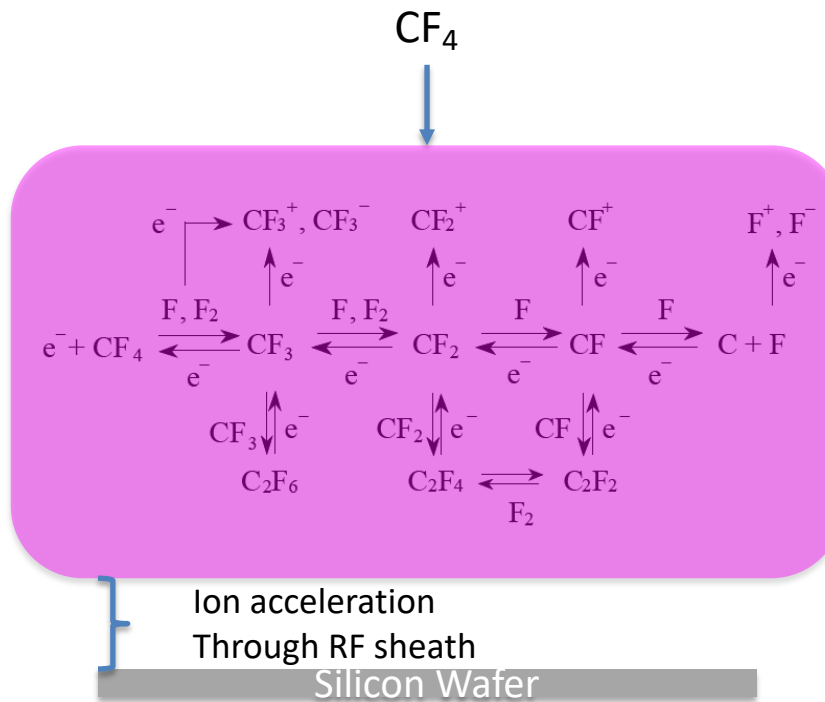
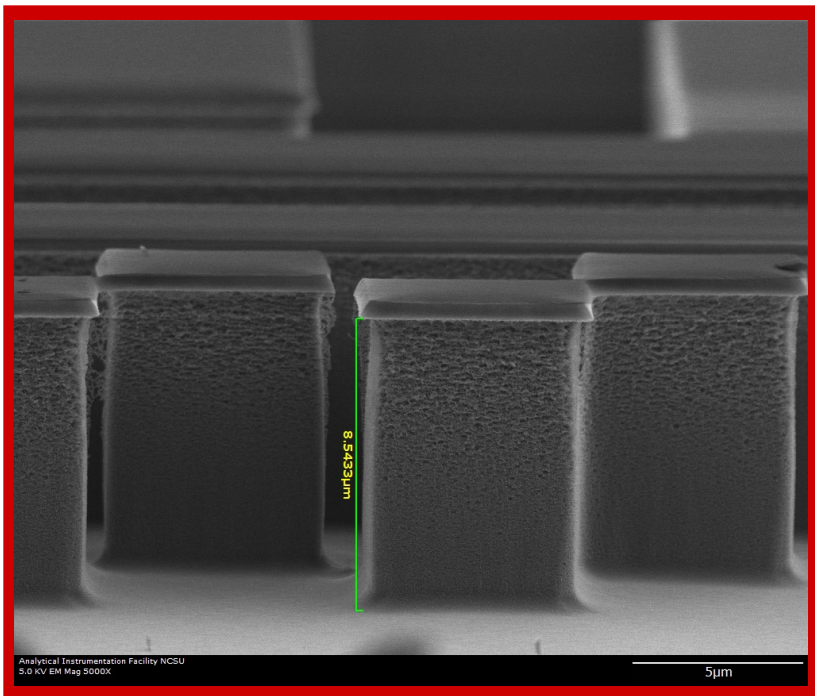


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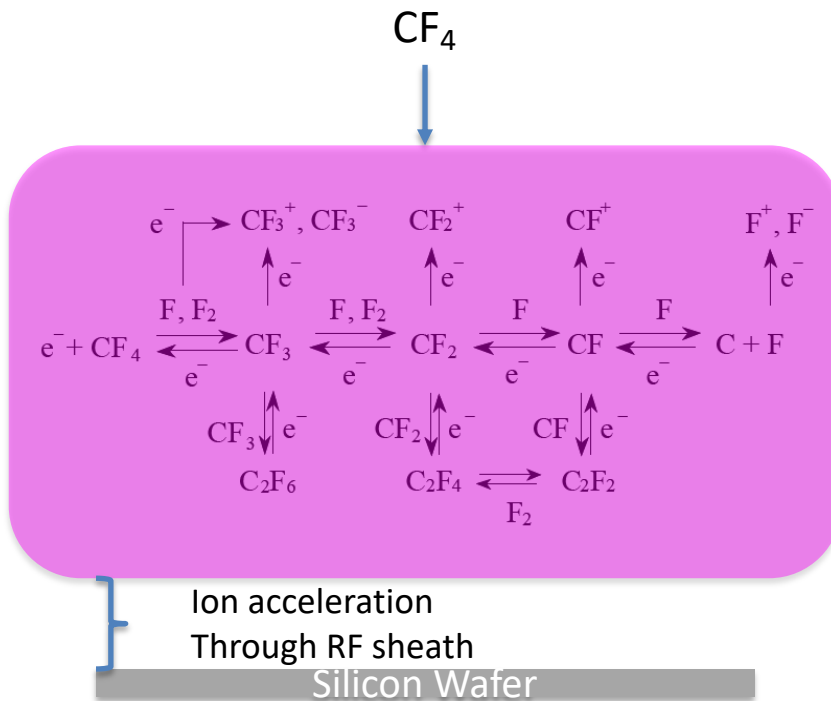
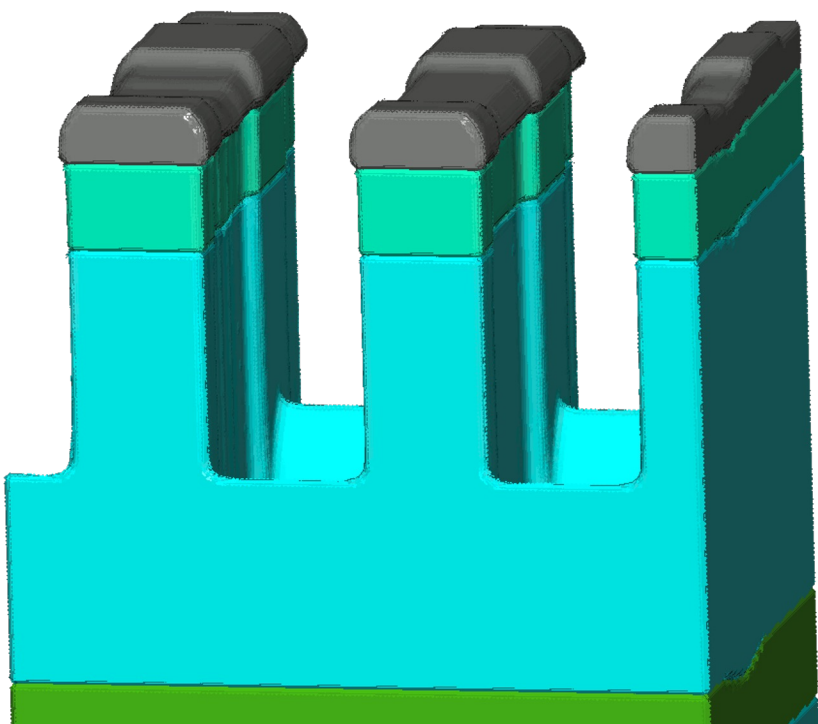


Fortunately this technology exists...



Applied Materials Advantage Etch System

Fortunately this technology exists...



Applied Materials Advantage Etch System

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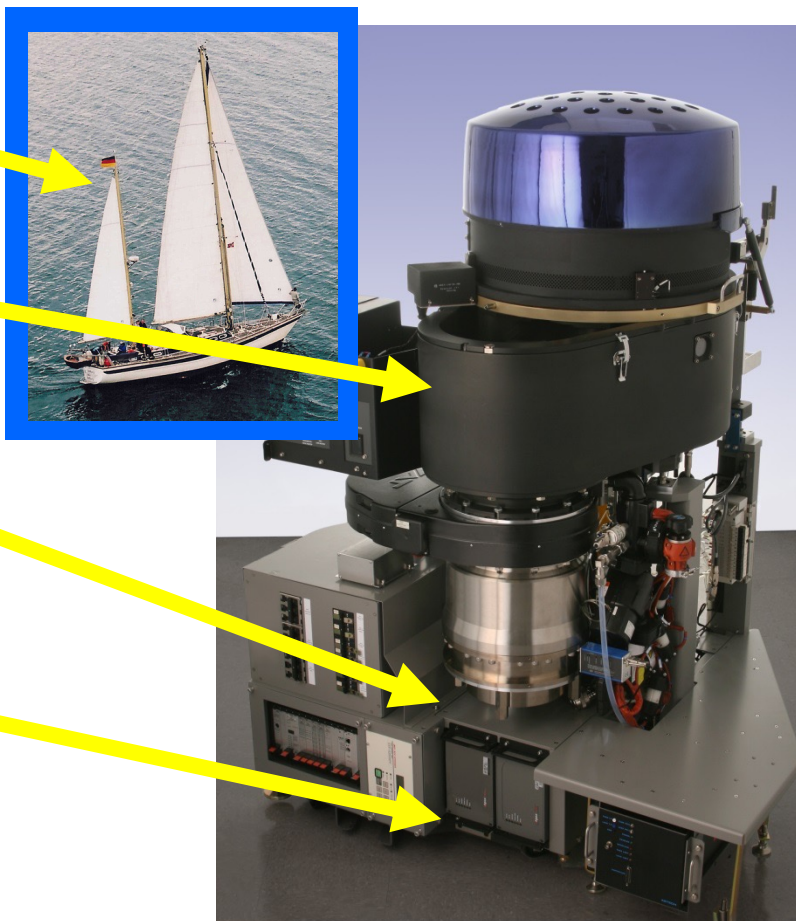
**Costs more than a 53 foot yacht
(~ \$1,000,000)**

**Has a vacuum chamber that can
provide the same conditions as
outer space
(base pressure < 1mTorr)**

**Turbo pump that spins faster than a
jet engine (~25,000 RPM)**

**More RF power than a college radio
station (~10,000 Watts)**

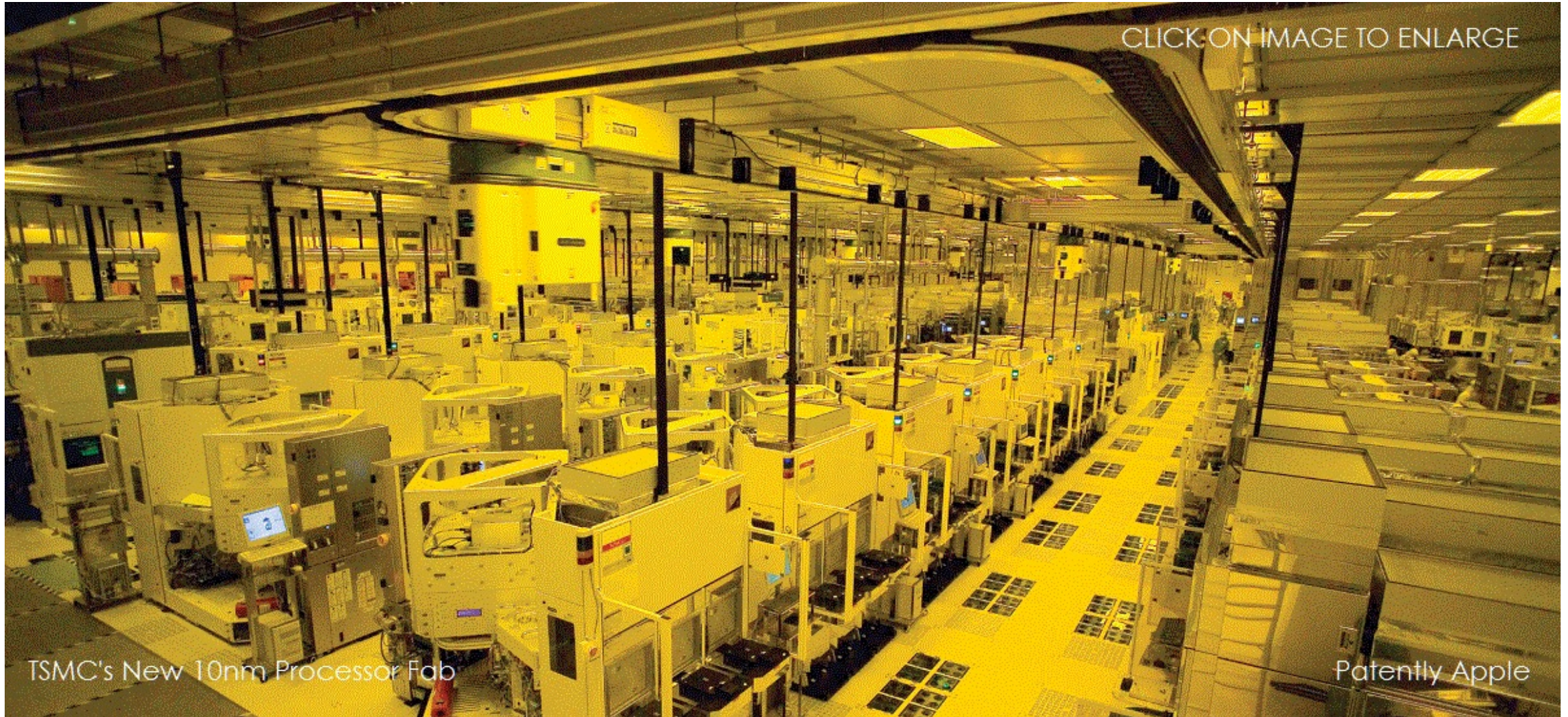
**Registered with the Federal
Communications Commission**



Applied Materials Advantage Etch System



Fortunately this technology exists...



CLICK ON IMAGE TO ENLARGE

TSMC's New 10nm Processor Fab

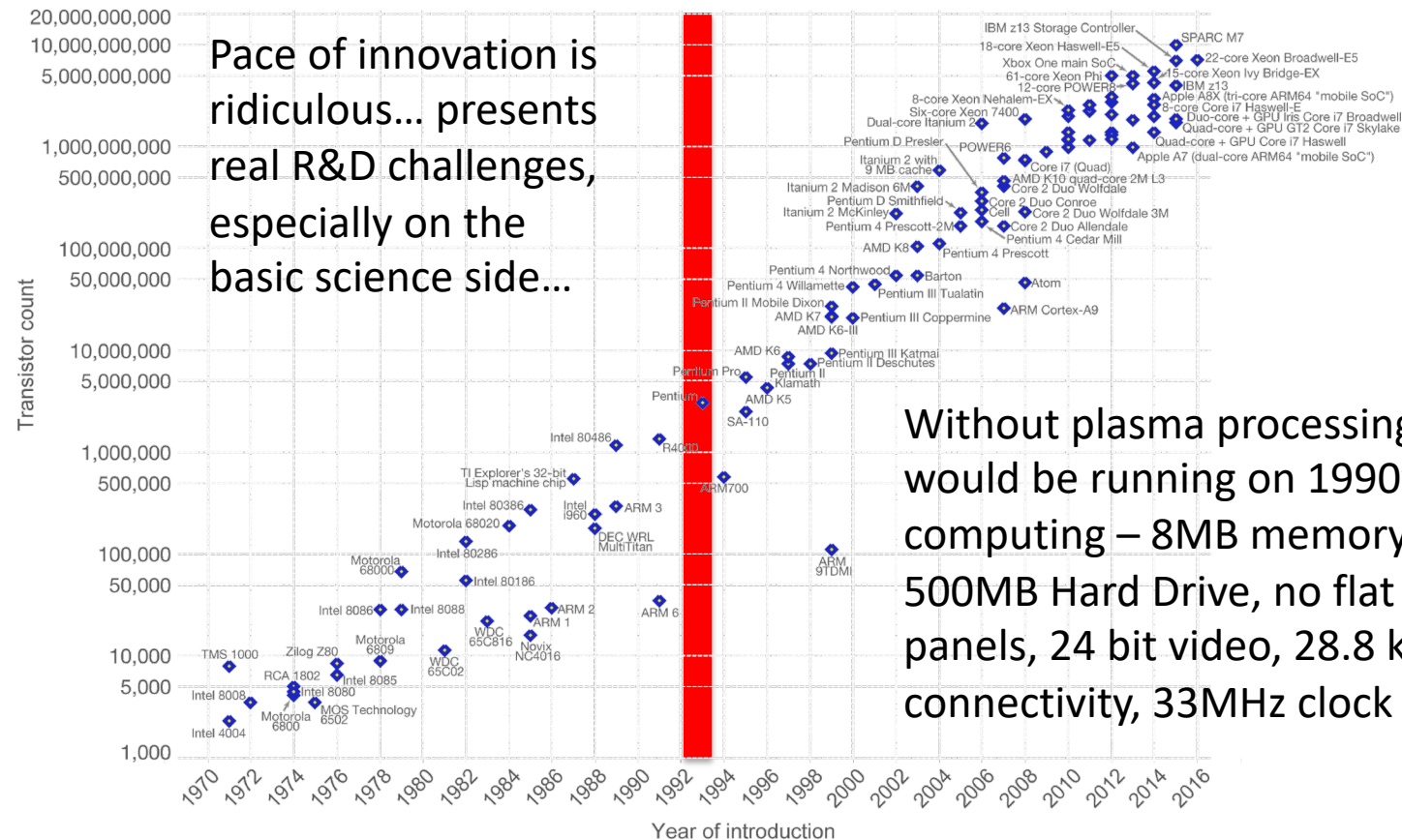
Patently Apple

Seriously.... Fortunately this technology exists...

Moore's Law – The number of transistors on integrated circuit chips (1971-2016)



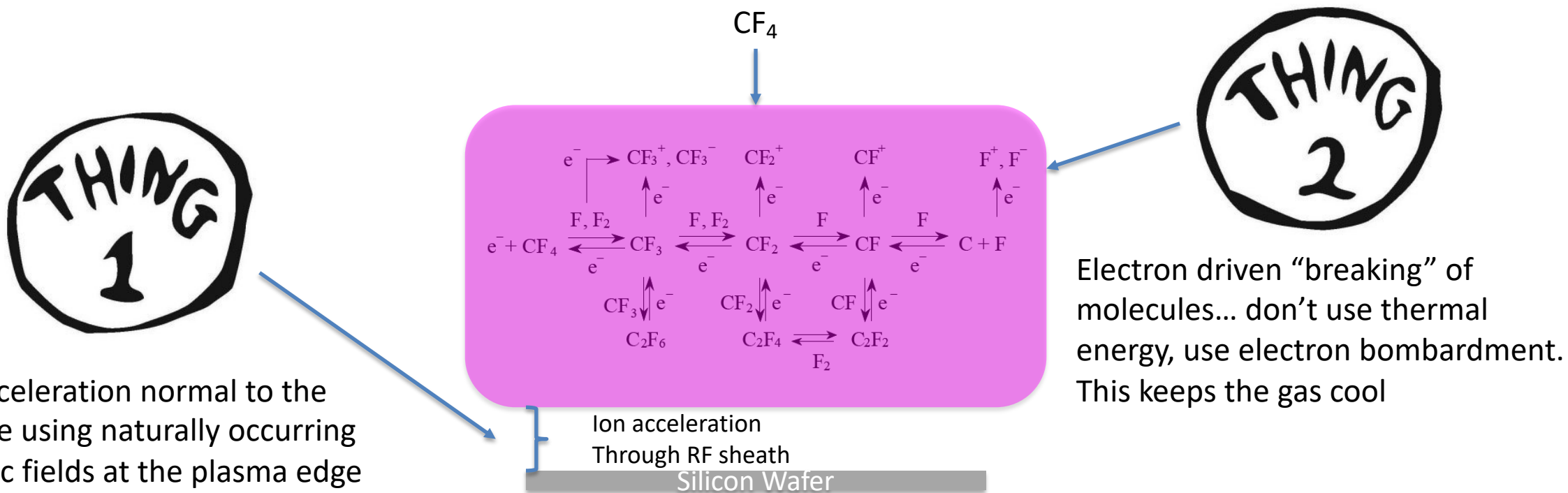
Moore's law describes the empirical regularity that the number of transistors on integrated circuits doubles approximately every two years. This advancement is important as other aspects of technological progress – such as processing speed or the price of electronic products – are strongly linked to Moore's law.



Data source: Wikipedia (https://en.wikipedia.org/wiki/Transistor_count)
 The data visualization is available at OurWorldinData.org. There you find more visualizations and research on this topic.

Licensed under CC-BY-SA by the author Max Roser.

So... how does it work? We need two things...

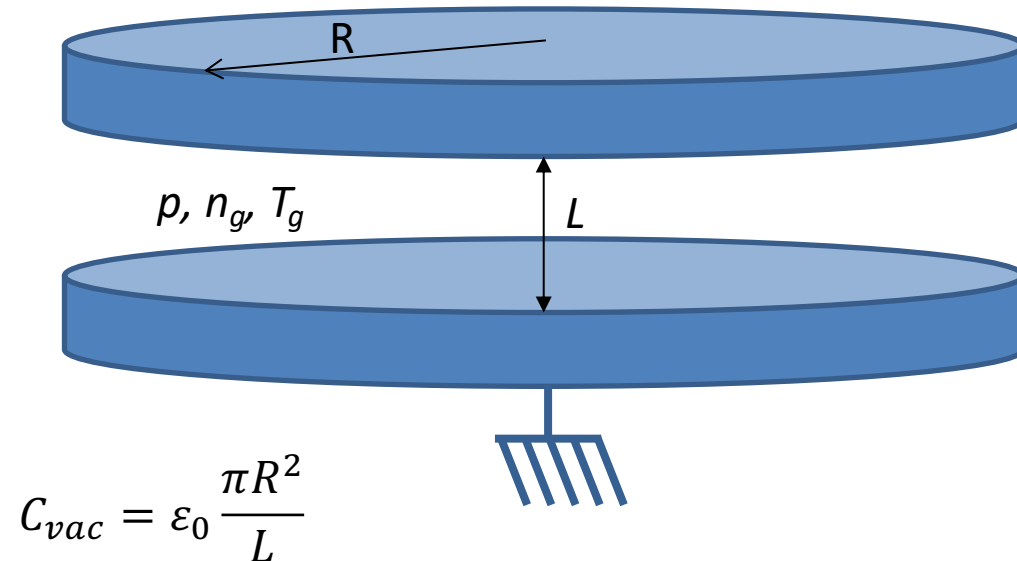


If I can combine electron impact driven chemistry and controlled ion bombardment, I have an anisotropic reactor!

Plasmas can do both!

Building a simple plasma reactor, which in its simplest form is basically a high voltage gas filled capacitor

Will try to keep this as simple as possible, but unfortunately at some point things have to get a little ugly, but not super ugly...



What happens if we fill this capacitor with a plasma?

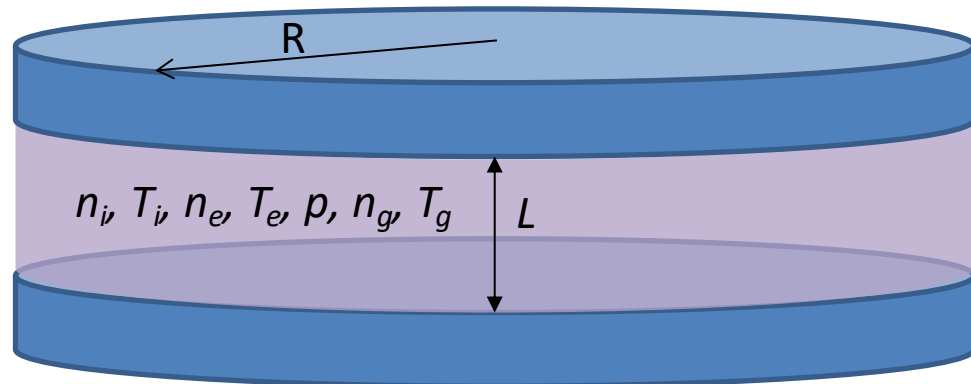
Note: most processing “plasmas” are still composed of around 99.9% neutral gas species

$$n_g = \frac{p}{kT_g} \approx 3 \times 10^{15} \text{ cm}^{-3} @ 100 \text{ mTorr } 300 \text{ K}$$

$$n_e = n_i \approx 10^8 \text{ cm}^{-3} - 10^{12} \text{ cm}^{-3} \text{ typically}$$

$$T_e \approx 2 \text{ eV} - 10 \text{ eV typically}$$

$$T_i \approx 0.03 \text{ eV} - 0.1 \text{ eV typically}$$



$$C_{vac} = \epsilon_0 \frac{\pi R^2}{L}$$

$$C_{load} = \left(\frac{L}{\epsilon_p \pi R^2} \right)^{-1}$$

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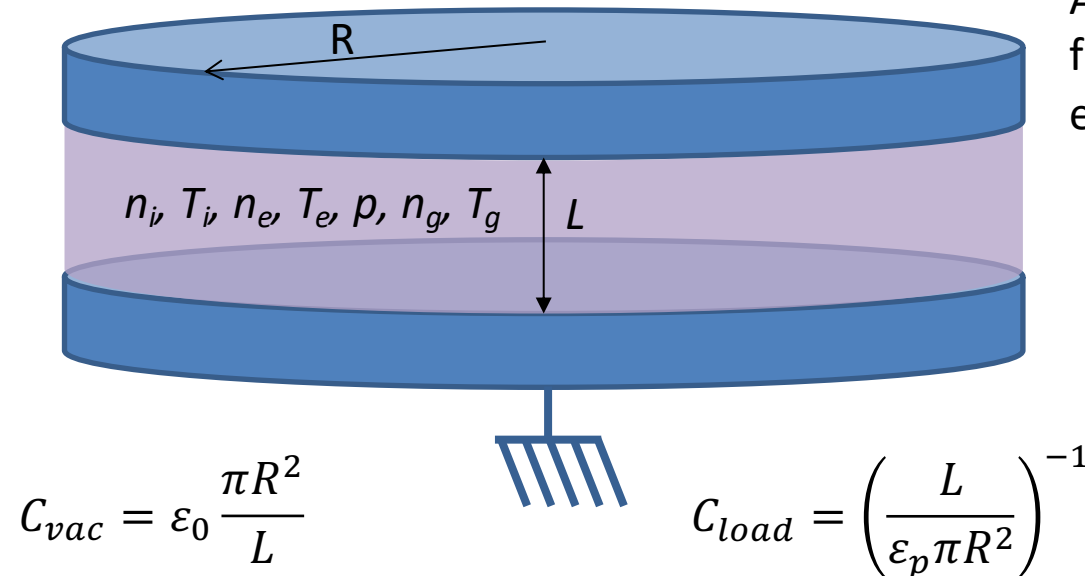
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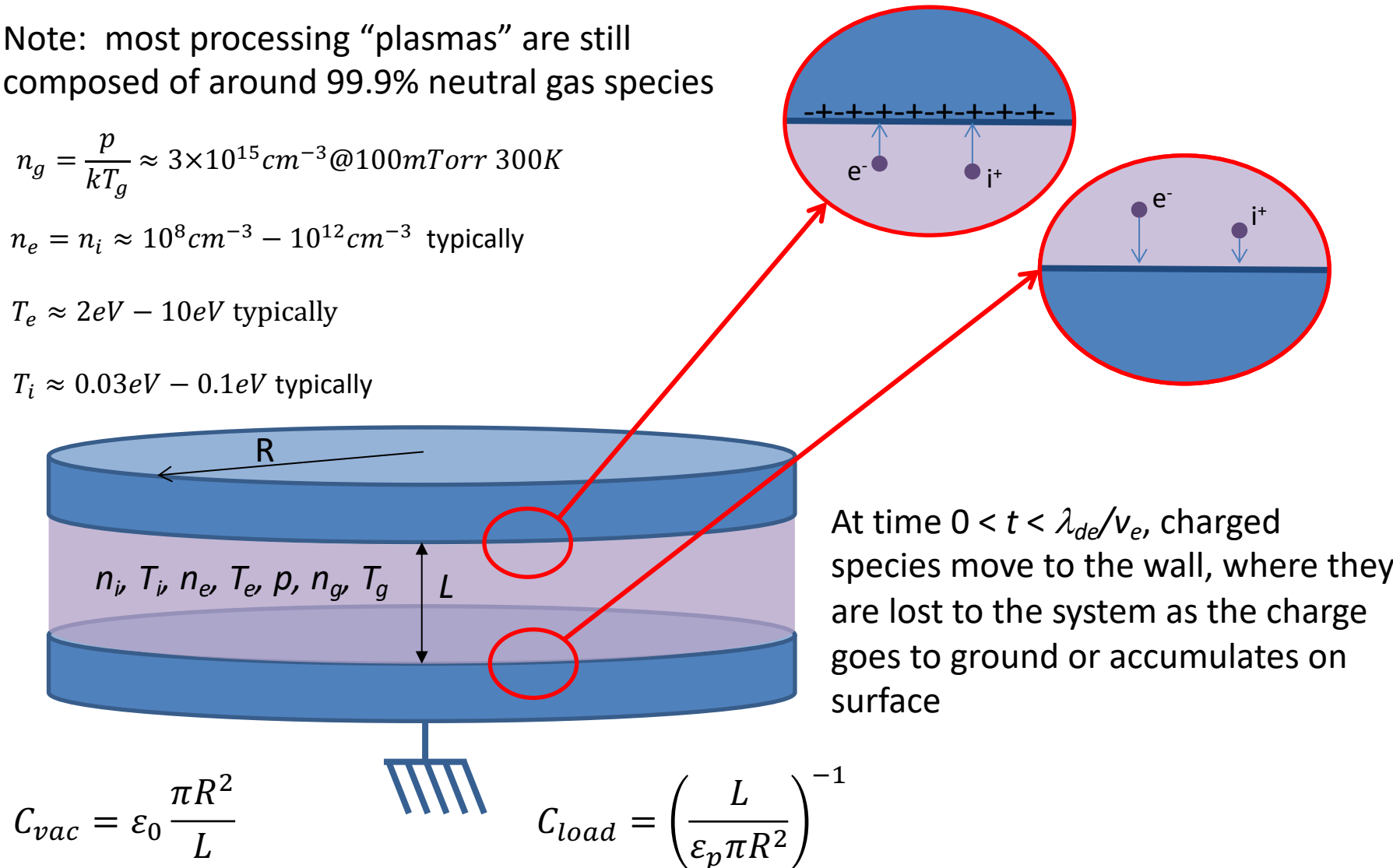
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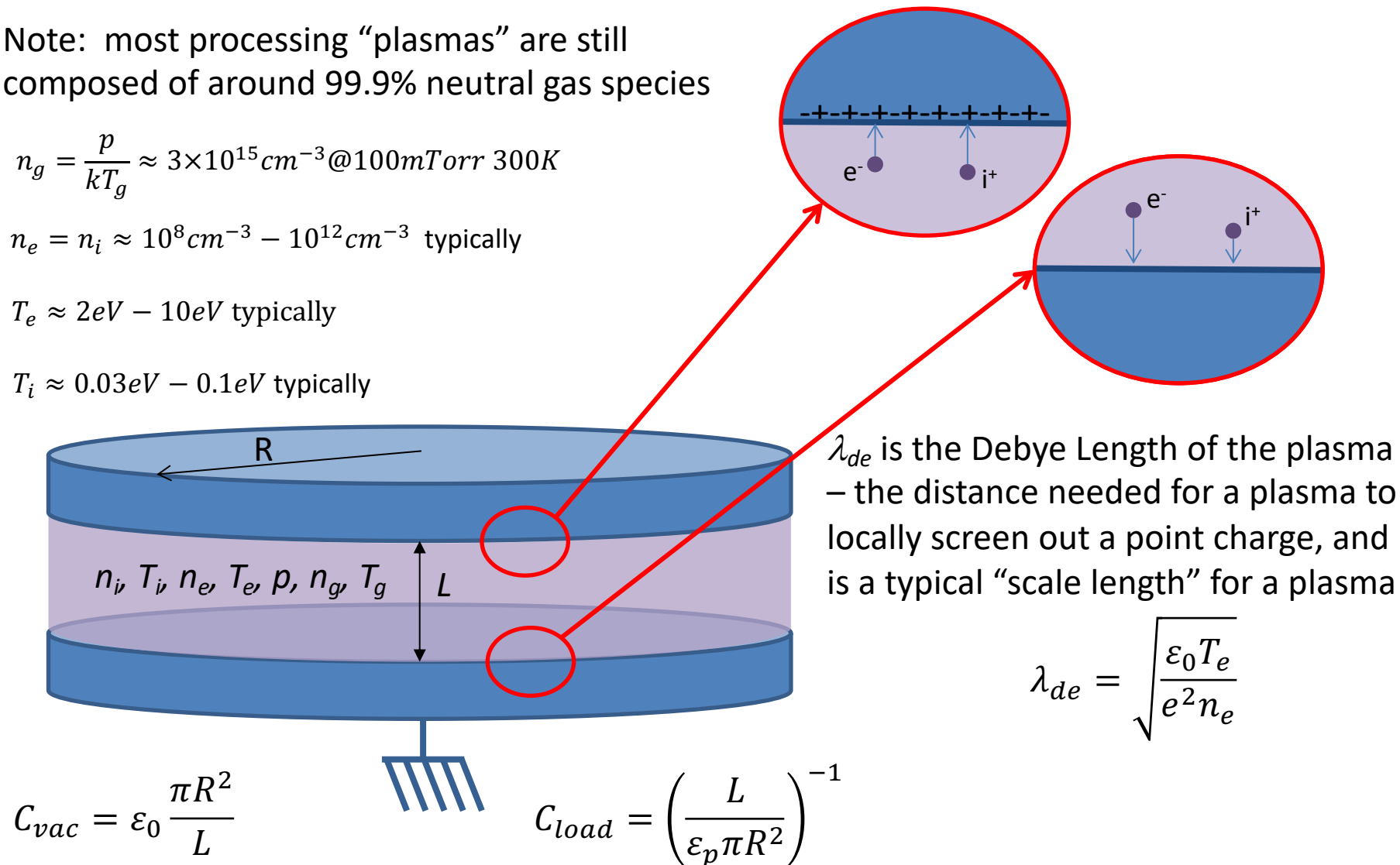
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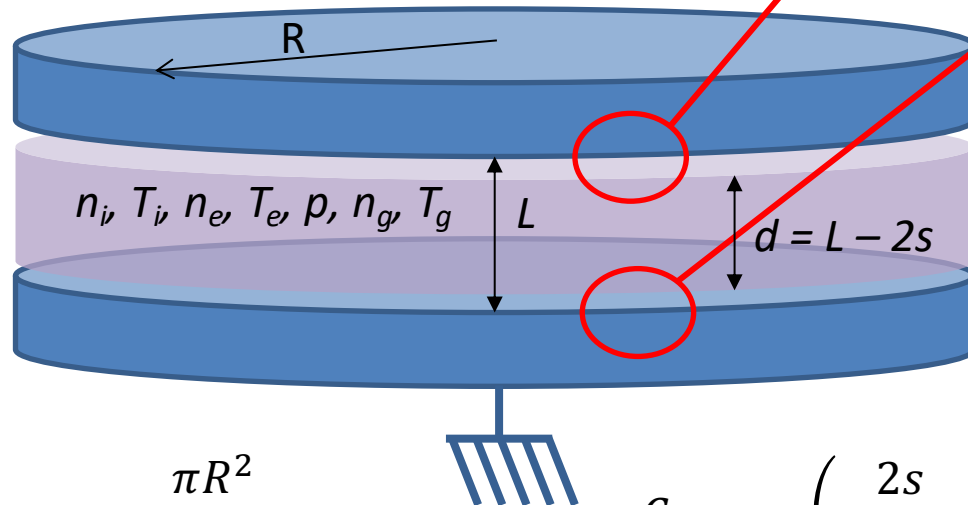
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At time $\lambda_{de}/v_e < t < \lambda_{de}/v_i$, Since electrons are thousands of times lighter than ions, they are more mobile and an electron depletion region forms around the surfaces

$$C_{vac} = \epsilon_0 \frac{\pi R^2}{L}$$

$$C_{load} = \left(\frac{2s}{\epsilon_0 \pi R^2} + \frac{L - 2s}{\epsilon_p \pi R^2} \right)^{-1}$$

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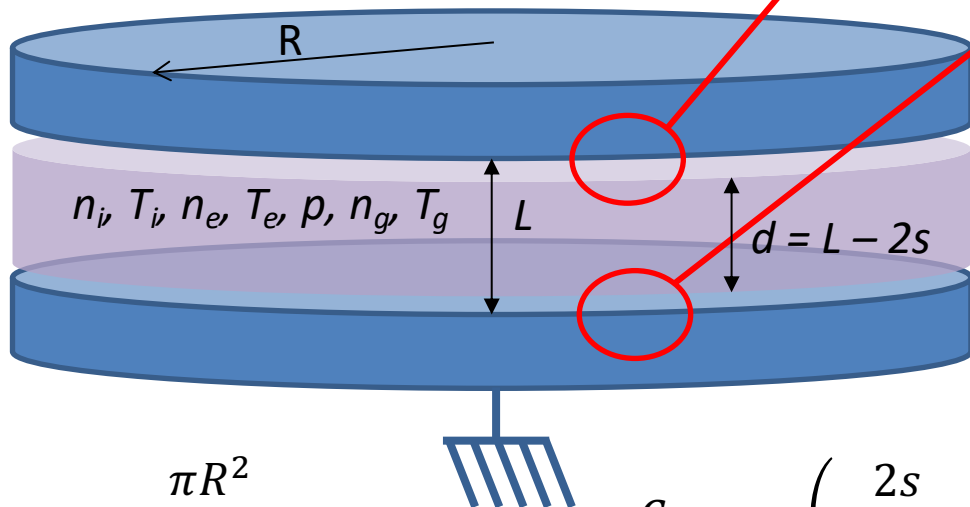
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At time $t > \lambda_{de}/v_i$ the electron depletion creates an electric field to zero diffusion current similar to the depletion region of a PN junction

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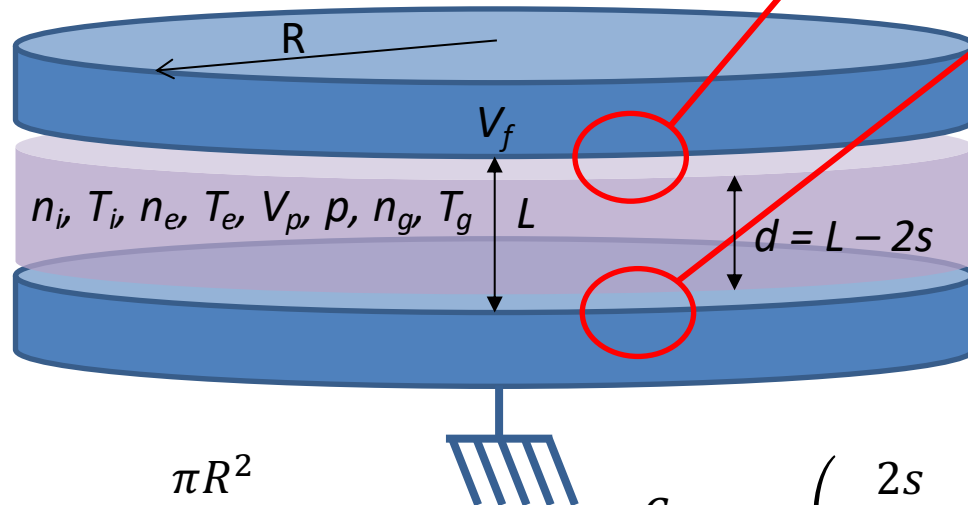
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$$\nabla \cdot \vec{E} = \nabla^2 V = \frac{\rho}{\epsilon} \approx -\frac{en_e}{\epsilon}$$

$$V_f = -T_e \ln \sqrt{\frac{m_{ion}}{2\pi m_e}} \sim -20 \text{ V in } 5 \text{ eV Ar}$$

$$V_p = \frac{m_{ion}}{2e} u_B^2 = \frac{m_{ion}}{2e} \frac{eT_e}{m_{ion}} = \frac{T_e}{2}$$

$$s \sim 0.5 \text{ mm } 5 \text{ eV Ar } 10^{10} \text{ cm}^{-3}$$

$$C_{vac} = \epsilon_0 \frac{\pi R^2}{L}$$

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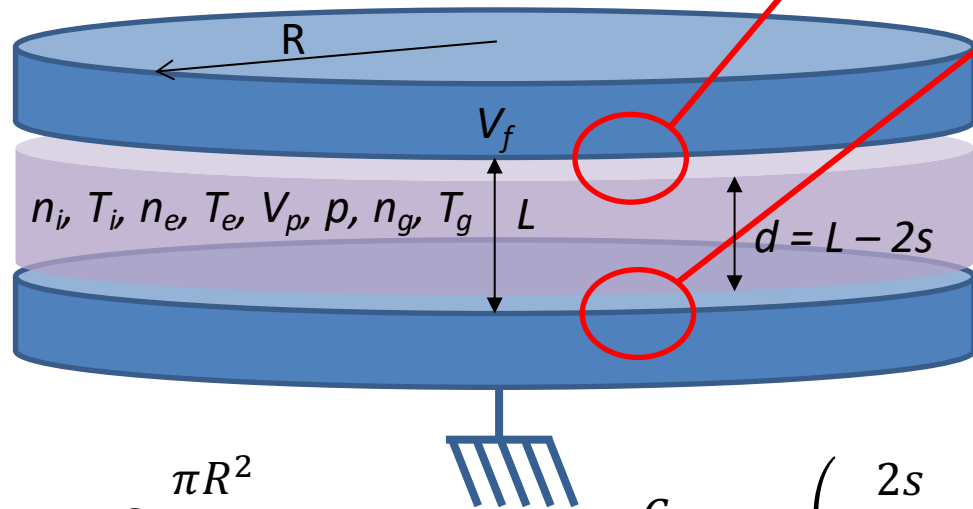
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The electric field accelerates ions normal to the surface, providing ion flux to ONLY horizontal surfaces and accelerating reactions on those surfaces

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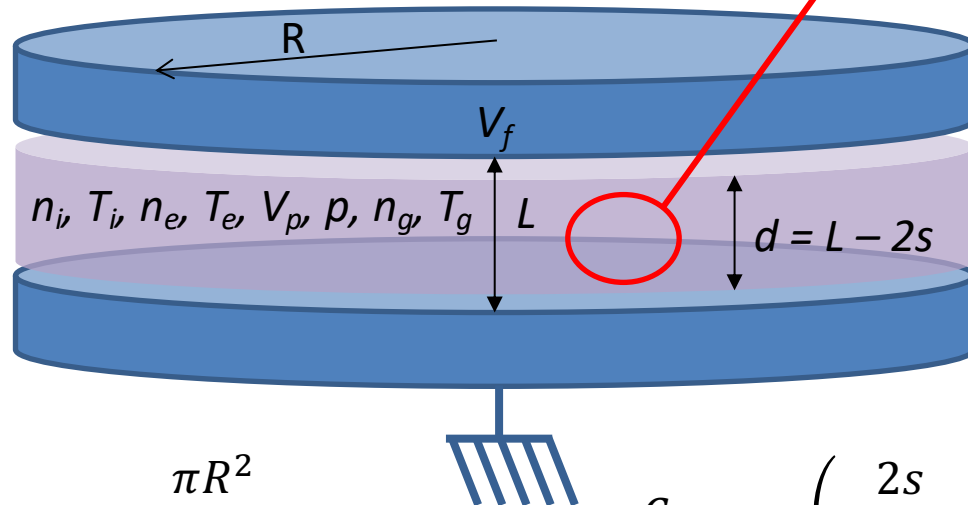
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Meanwhile, in the bulk plasma region, the faster electrons collide mainly with neutral gas species

- Elastic collisions (polarization scattering)
- Inelastic collisions – excitation, dissociation
- Ionization collisions – have a threshold energy, produce more *e-i* pairs

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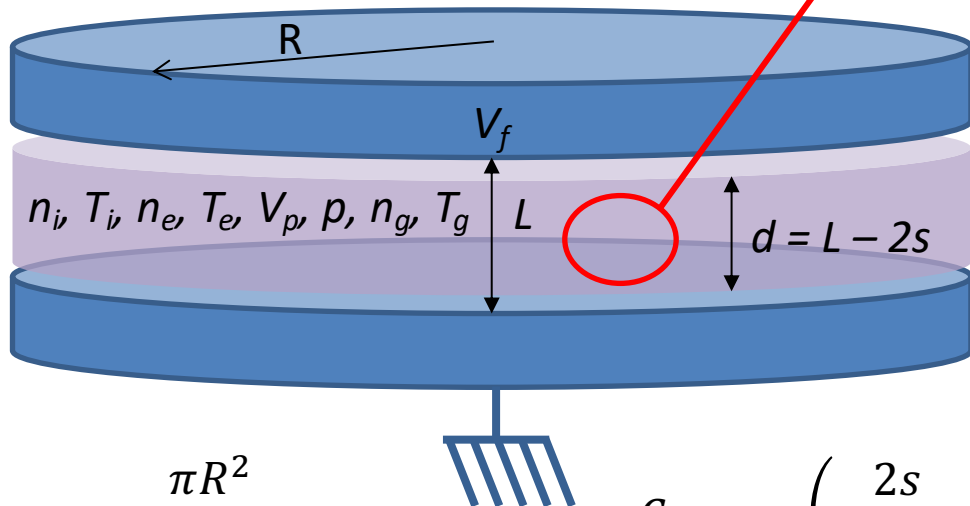
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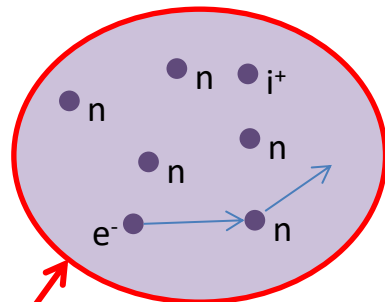
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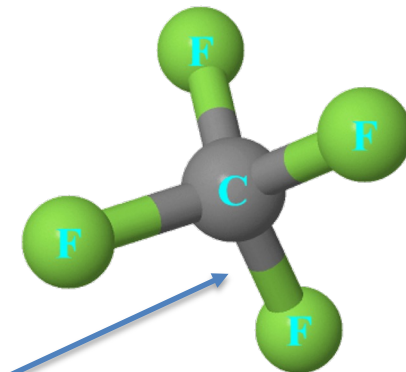


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$E > 5 \text{ eV}$



C-F bond energy
~5eV

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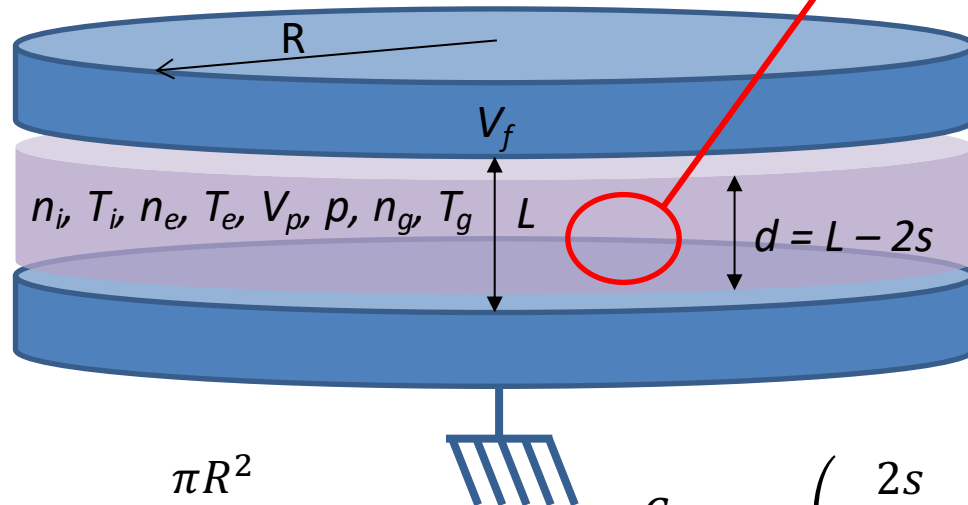
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$$n_g = \frac{p}{kT_g} \approx 3 \times 10^{15} \text{ cm}^{-3} @ 100 \text{ mTorr } 300 \text{ K}$$

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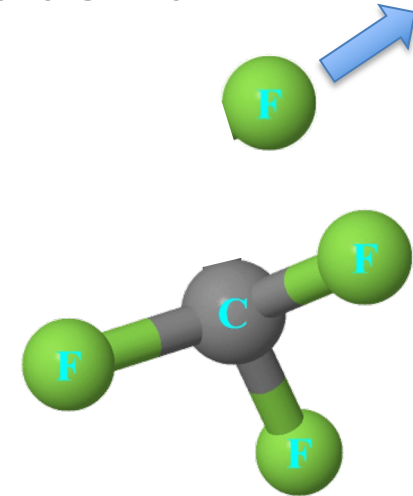
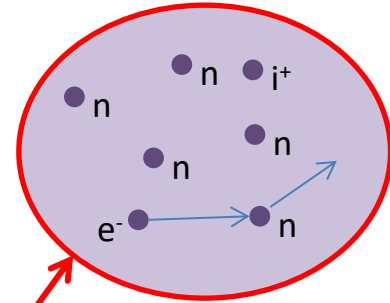
$$T_e \approx 2 \text{ eV} - 10 \text{ eV typically}$$

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$$C_{vac} = \epsilon_0 \frac{\pi R^2}{L}$$

$$C_{load} = \left(\frac{2s}{\epsilon_0 \pi R^2} + \frac{L - 2s}{\epsilon_p \pi R^2} \right)^{-1}$$



$E < 5 \text{ eV}$



Meanwhile, in the bulk plasma region, the faster electrons collide mainly with neutral gas species

- Elastic collisions (polarization scattering)
- Inelastic collisions – excitation, dissociation
- Ionization collisions – have a threshold energy, produce more $e-i$ pairs

What happens if we fill this capacitor with a plasma?

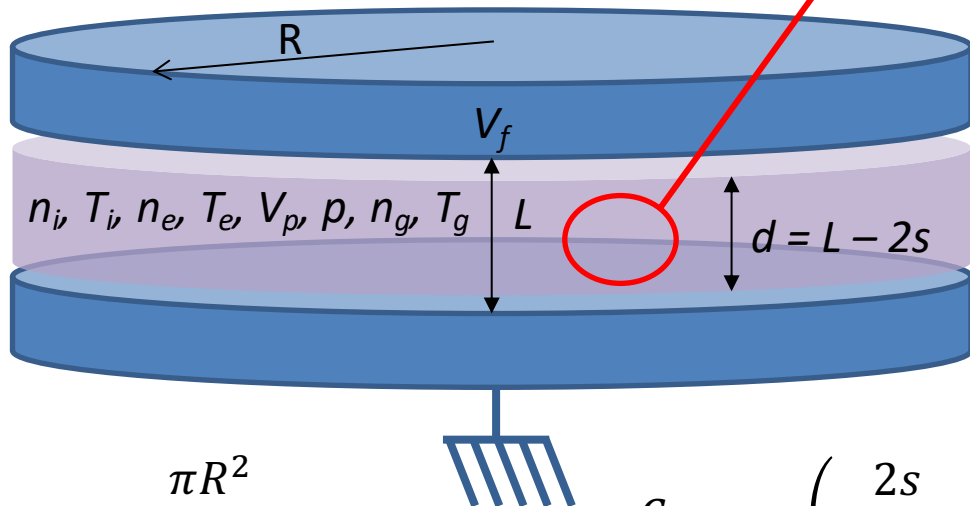
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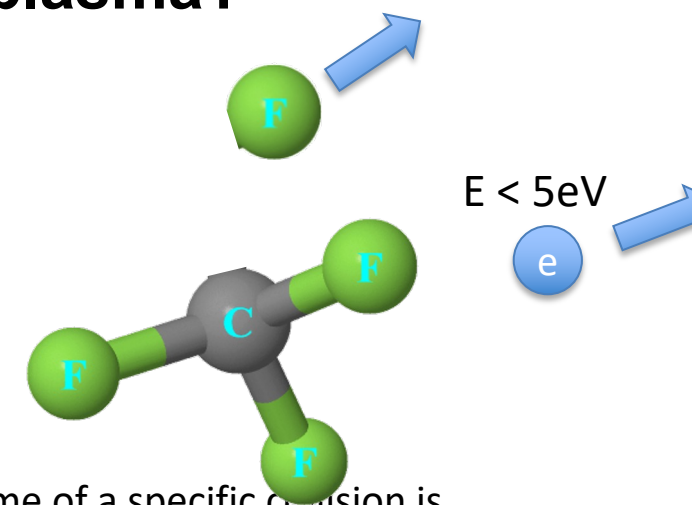
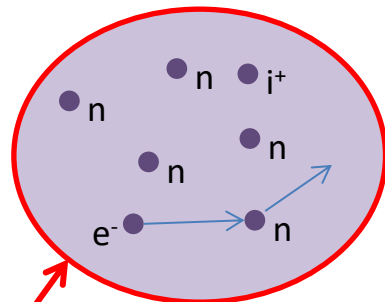
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The rate per unit volume of a specific collision is determined by four factors:

1. The number of electrons n_e
2. The number of targets for the electron to hit n_{target}
3. The velocity of the electron $(2E_e/m_e)^{1/2}$
4. The effective size of the target atom or molecule for that collision, the cross section σ

What happens if we fill this capacitor with a plasma?

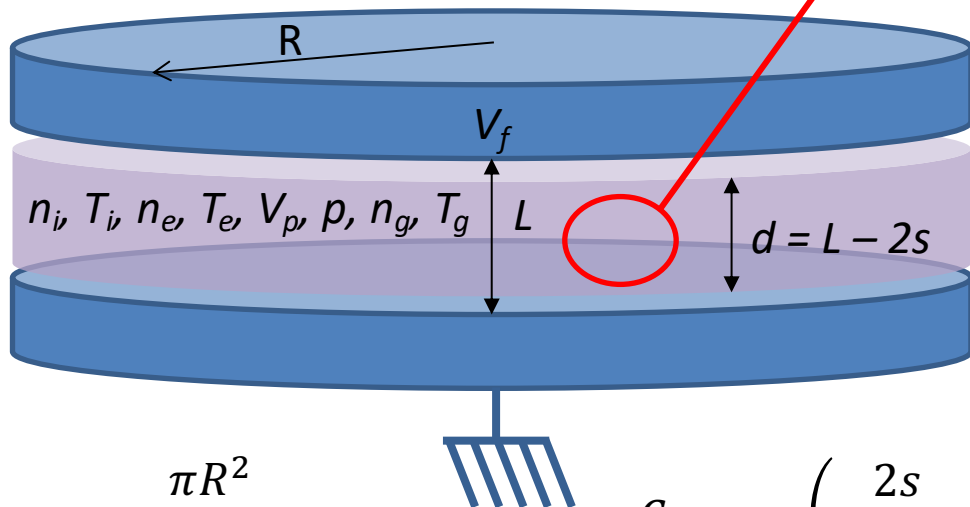
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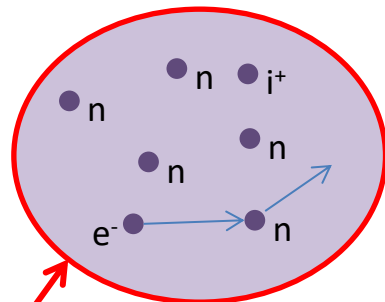
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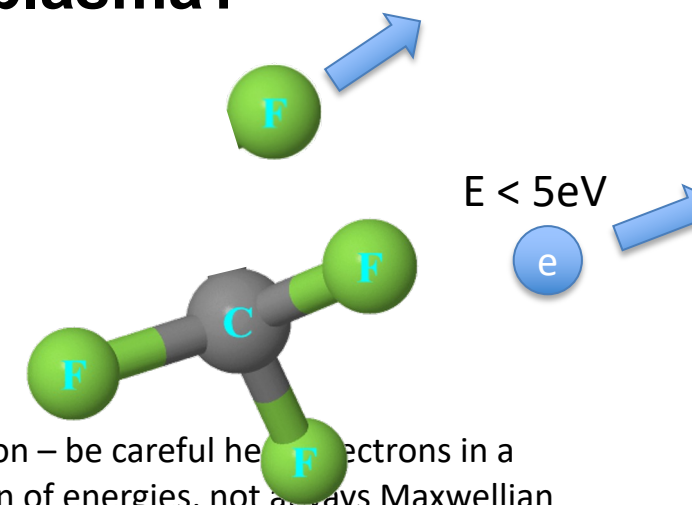


$$C_{vac} = \epsilon_0 \frac{\pi R^2}{L}$$

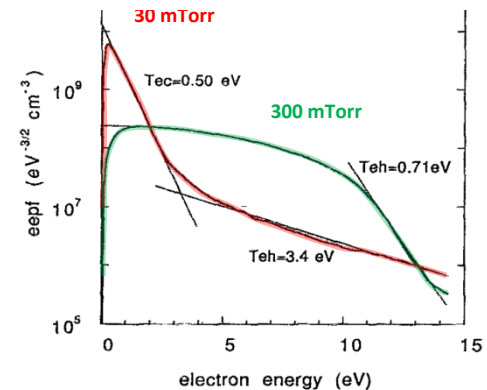
$$C_{load} = \left(\frac{2s}{\epsilon_0 \pi R^2} + \frac{L - 2s}{\epsilon_p \pi R^2} \right)^{-1}$$



The velocity of the electron – be careful here! Electrons in a plasma have a distribution of energies, not always Maxwellian



J. Appl. Phys. **73** (8), 1993 3657-3664



What happens if we fill this capacitor with a plasma?

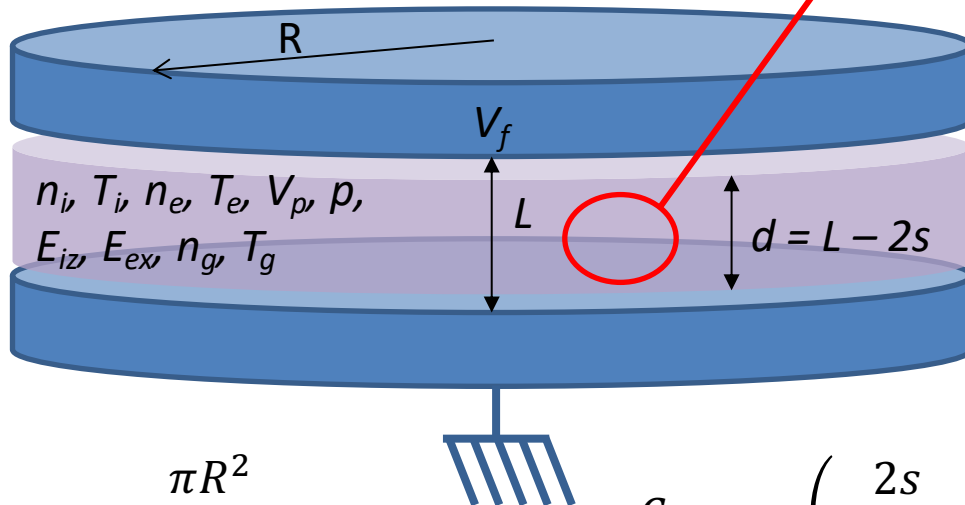
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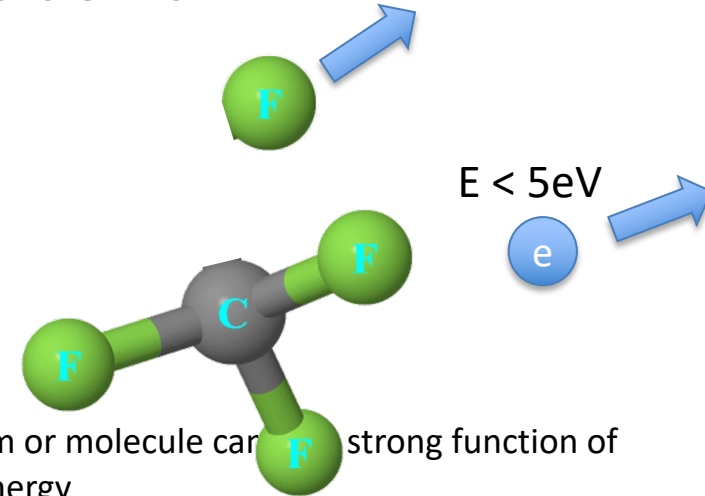
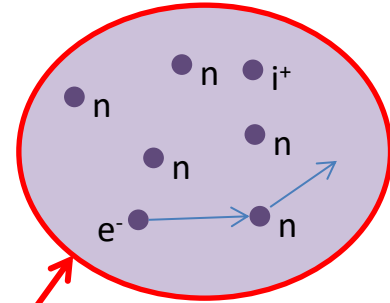
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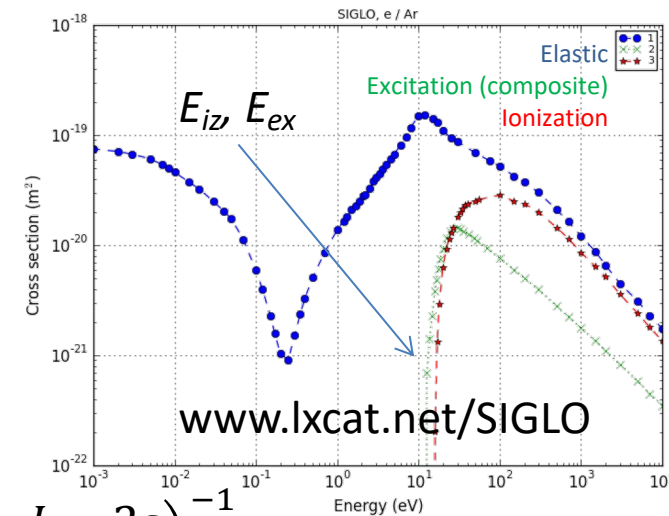


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$$C_{load} = \left(\frac{2s}{\epsilon_0 \pi R^2} + \frac{L - 2s}{\epsilon_p \pi R^2} \right)^{-1}$$



The target size of the atom or molecule can have a strong function of an individual electron's energy



What happens if we fill this capacitor with a plasma?

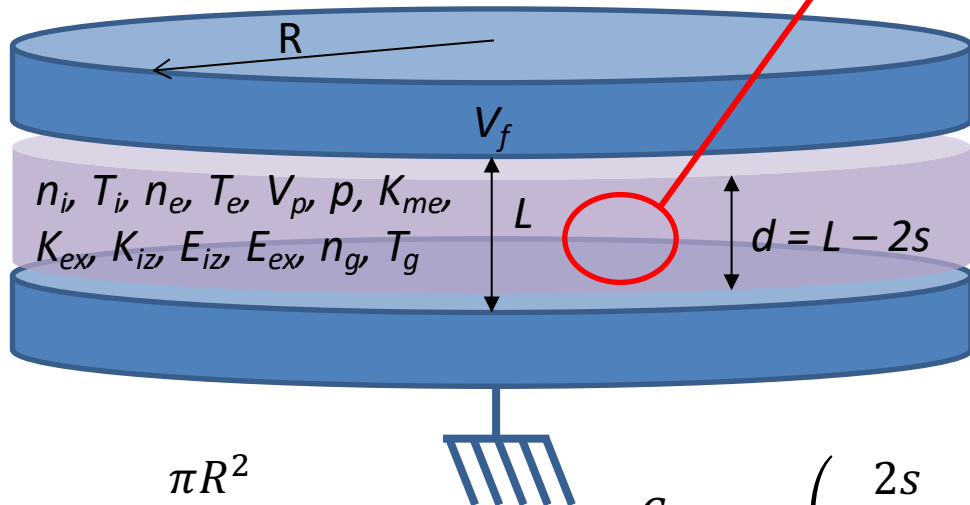
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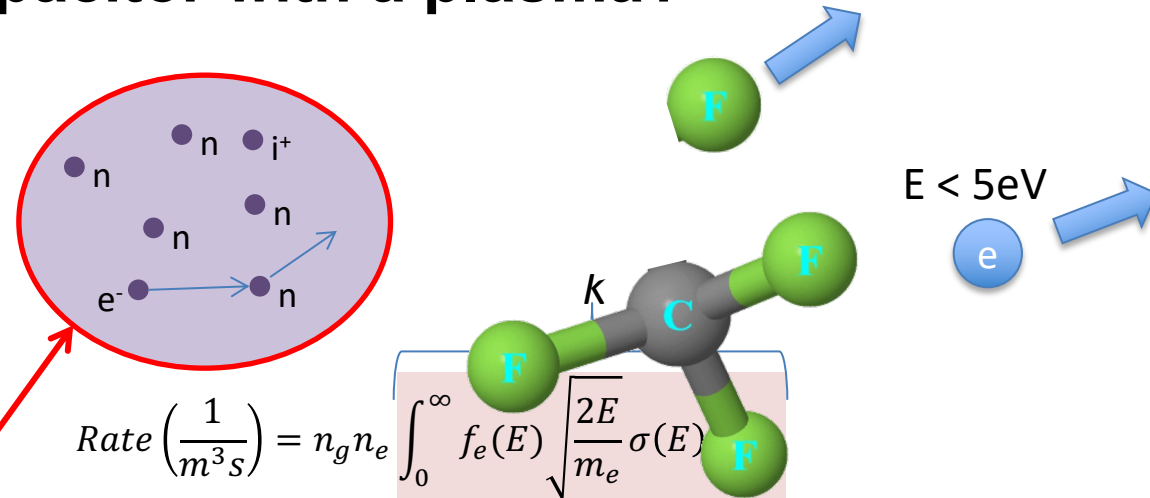
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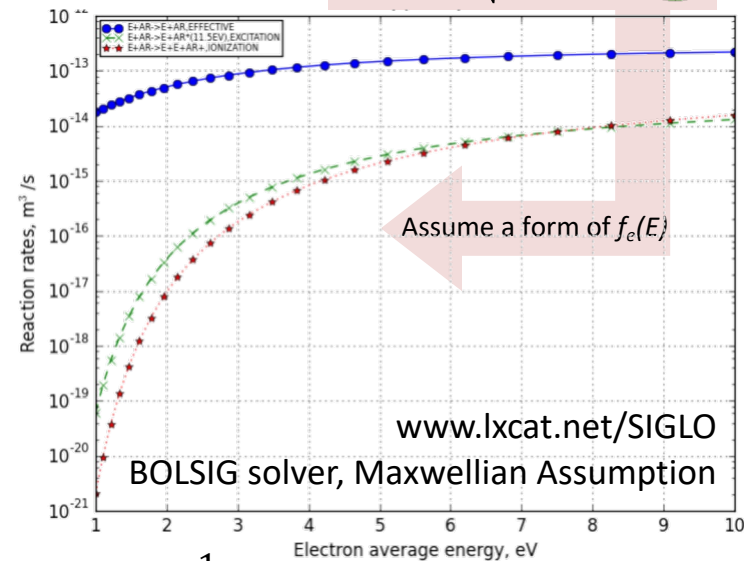


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$$\text{Rate} \left(\frac{1}{\text{m}^3 \text{ s}} \right) = n_g n_e \int_0^\infty f_e(E) \sqrt{\frac{2E}{m_e}} \sigma(E)$$



What happens if we fill this capacitor with a plasma?

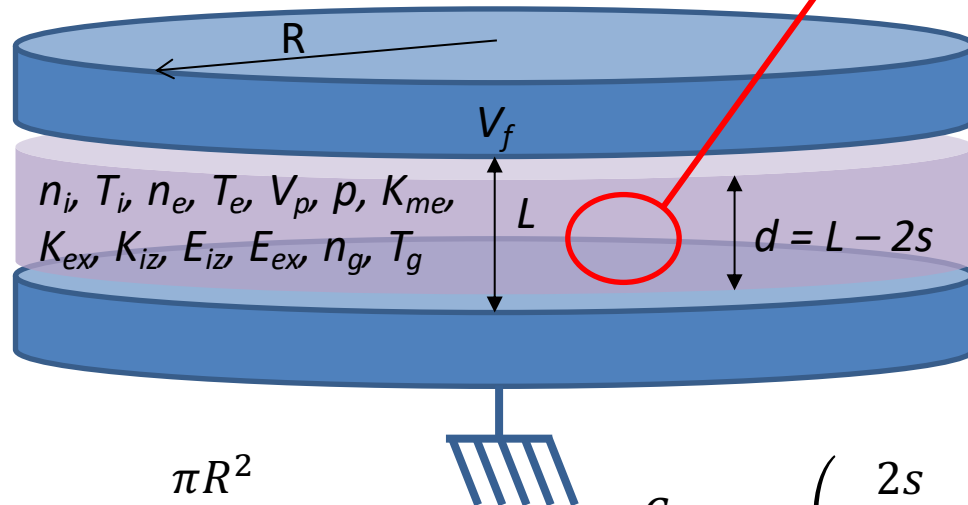
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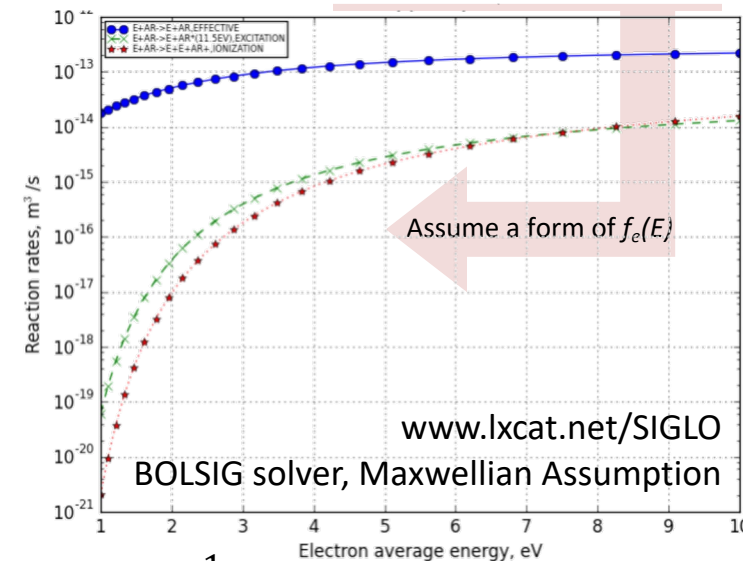
$$T_i \approx 0.03 \text{ eV} - 0.1 \text{ eV typically}$$



This gives us reaction rates (K), just like in chemistry, but they are a function of the electron’s temperature, NOT the gas temperature

But – we do get reactive gas species without heating up the background gas

Rate $\left(\frac{-}{n}\right)$ much



$$C_{vac} = \epsilon_0 \frac{\pi R^2}{L}$$

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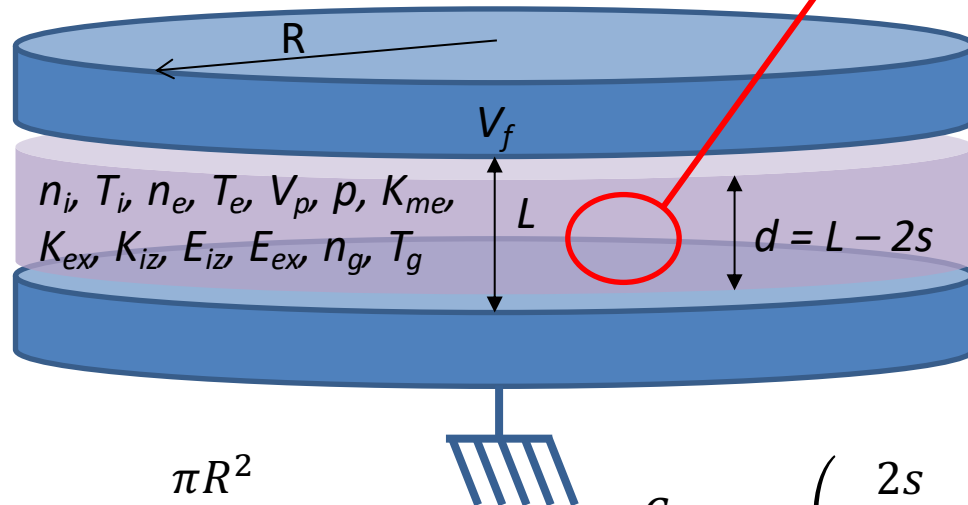
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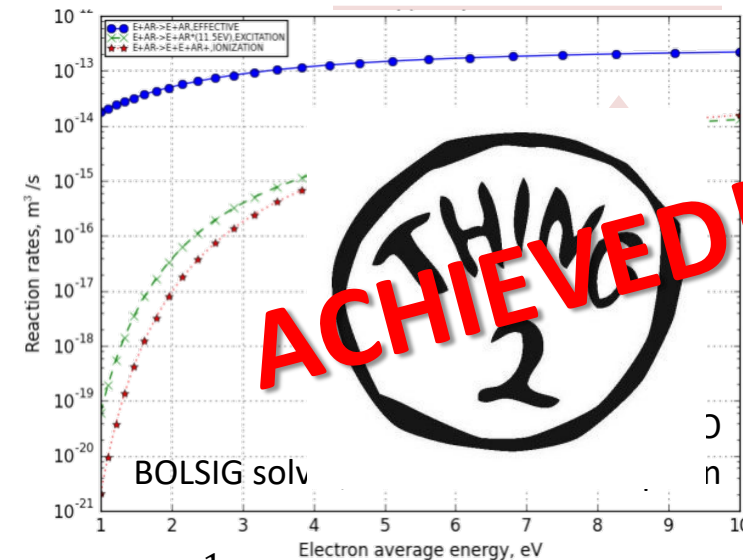


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This gives us reaction rates (K), just like in chemistry, but they are a function of the electron’s temperature, NOT the gas temperature

But – we do get reactive gas species without heating up the background gas much and we can control it with electron temperature



However - the list of reactions gets very long, and very difficult to set up and solve balance equations

Number	Reaction	Rate Constant (cm ³ /s)	Source
<i>Reactions among e, O₂, O₂⁺, O, and O⁻</i>			
1	e + O ₂ momentum transfer	4.7E-8T _e ^{0.5}	a
2	e + O ₂ → O ⁻ + O	1.07E-9T _e ^{1.391} exp(-6.26/T _e)	j
3	e + O ₂ → 2O + e	6.86E-9exp(-6.29/T _e)	g2
4	e + O ₂ → O ₂ ⁺ + 2e	2.34E-9T _e ^{1.03} exp(-12.29/T _e)	kr
5	e + O ⁻ → O + 2e	5.47E-8T _e ^{0.324} exp(-2.98/T _e)	vc
6	e + O ₂ ⁺ → 2O	2.2E-8/T _e ^{1/2}	g3
7	O ⁻ + O ₂ ⁺ → O + O ₂	2.6E-8(300/T) ^{0.44}	g3
8	O ⁻ + O → O ₂ + e	(1.9, 3, 5)E-10	h,m,k
9	O ⁻ + O ₂ ⁺ → 3O	2.6E-8(300/T) ^{0.44}	g3
<i>Addition of O⁺</i>			
10	e + O ₂ → O ⁻ + O ⁺ + e	7.1E-11T _e ^{0.5} exp(-17/T _e)	r
11	e + O ₂ → O + O ⁺ + 2e	1.88E-10T _e ^{1.699} exp(-16.81/T _e)	kr
12	e + O → O ⁺ + 2e	9.0E-9T _e ² exp(-13.6/T _e)	d
13	O ⁻ + O ⁺ → 2O	4.0E-8(300/T) ^{0.44}	g3
14	O ⁺ + O ₂ → O + O ₂ ⁺	2.0E-11(300/T) ^{0.5}	e
<i>Addition of metastable O₂^(1Δg); see note f below</i>			
15	e + O ₂ → O ₂ ⁺ + e	1.37E-9 exp(-2.14/T _e)	g2
16	e + O ₂ ⁺ → e + O ₂	2.06E-9 exp(-1.163/T _e)	b
17	e + O ₂ ⁺ → O + O ⁻	4.19E-9T _e ^{1.376} exp(-5.19/T _e)	j
18	O ₂ ⁺ + O ₂ → 2O ₂	2.2E-18(7300) ^{0.8}	e,k
19	O ₂ ⁺ + O → O ₂ + O	(1.0, 7)E-16	e,k
20	O ⁻ + O ₂ ⁺ → O ₃ + e	2.2E-11	g0
21	O ⁻ + O ₂ ⁺ → O ₂ ⁻ + O	1.1E-11	g0
<i>Addition of metastable O(^{1D})</i>			
22	e + O ₂ → O + O ⁺ + e	3.49E-8 exp(-5.92/T _e)	g2
23	e + O → O ⁺ + e	4.54E-9 exp(-2.36/T _e)	g2
24	e + O ⁺ → e + O	8.17E-9 exp(-0.4/T _e)	b
25	e + O ⁺ → O ⁺ + 2e	9.0E-9T _e ^{2.7} exp(-11.6/T _e)	d
26	O ⁺ + O → 2O	8.0E-12	e
27	O ⁺ + O ₂ → O + O ₂	(6.4, 7.0)E-12 exp(67/T)	k,e
28	O ⁺ + O ₂ → O + O ₂ ⁺	1.0E-12	e
<i>Addition of selected reactions for O₂⁻ and O₃</i>			
29	O ⁻ + O ₂ → O ₃ + e	5E-15	k
30	e + O ₃ → O ₂ ⁻ + O	1E-9	k
31	e + O ₃ → O ⁻ + O ₂	2.12E-9T _e ^{-1.058} exp(-0.93/T _e)	s
32	O ₂ ⁻ + O ₂ ⁺ → 2O ₂	2E-7(300/T) ^{0.5}	k
33	O ₂ ⁻ + O ⁺ → O ₂ + O	(1, 2)E-7(300/T) ^{0.5}	e,k
34	O ₃ + O ₂ → O ₂ + O + O ₂	7.3E-10exp(-11400/T)	e
35	O ₃ + O → 2O ₂	1.8E-11exp(-2300/T)	e

Note: T_e in volts and T in kelvins. Two values from different sources are sometimes given in parentheses. The notation E-8 means 10⁻⁸.
^aBased on Phelps (1985); ^bBased on detailed balance; ^cBased on Rangwala et al. (1999).
^dBased on Lee et al. (1994); ^eEliasson and Kogelschatz (1986).
^fReactions 1, 3, 4, 10, 11 for O₂⁺ have activation energies reduced by ~1 V.
^{g0}Gudmundsson et al. (2000); ^{g1}Gudmundsson et al. (2001); ^{g2}Gudmundsson (2002).
^{g3}Gudmundsson (2004); ^hFehsenfeld (1967).
^jBased on Jaffke et al (1992); ^kKossyi et al. (1992); ^mSommerer and Kushner (1992).
^lBased on Krishnakumar and Srivastava (1992); ⁿBased on Rapp and Briglia (1965).
^vBased on Vejby-Christensen et al. (1996); ^wBased on Senn et al. (1999).

- Imagine the list of pertinent reactions for something like SF₆, CF₄, C₄F₈, or Si(OC₂H₅)₄ (TEOS)
- Even worse, realize that rarely is only one gas used for a process. Dielectric etch would run Ar, O₂, and C₄F₈ at the same time.
- And even if you could build a complete set of reactions, the cross sections and rate constants for many of these species are at best “qualitative”

And the list of reactions gets very very long, and very difficult to set up and solve balance equations

624 Reactions!

Table with 20 columns: Index, Reaction, Rate constant, Index, Reaction, Rate constant, Index, Reaction, Rate constant, Index, Reaction, Rate constant, Index, Reaction, Rate constant, Index, Reaction, Rate constant, Index, Reaction, Rate constant, Index, Reaction, Rate constant. The table lists 624 nuclear reactions with their corresponding rate constants.

And the list of reactions gets very very long, and very difficult to set up and solve balance equations

Electron Impact Driven

Boltzmann Reactions

624 Reactions!
Positive (and negative) Ion Driven Reactions

Excited Atomic and Molecular Specie Driven

Index	Reaction	Rate constant*	Index	Reaction	Rate constant*	Index	Reaction	Rate constant*	Index	Reaction	Rate constant*	Index	Reaction	Rate constant*	Index	Reaction	Rate constant*
(001)	$e + N_2 \rightarrow N_2^+ + 2e$	$5.39 \times 10^{-18} \exp(-9.161/T_e)$	(121)	$e + N_2 \rightarrow N_2^+ + 2e$	$5.39 \times 10^{-18} \exp(-9.161/T_e)$	(241)	$e + N_2 \rightarrow N_2^+ + 2e$	$5.39 \times 10^{-18} \exp(-9.161/T_e)$	(361)	$e + N_2 \rightarrow N_2^+ + 2e$	$5.39 \times 10^{-18} \exp(-9.161/T_e)$	(481)	$e + N_2 \rightarrow N_2^+ + 2e$	$5.39 \times 10^{-18} \exp(-9.161/T_e)$	(601)	$e + N_2 \rightarrow N_2^+ + 2e$	$5.39 \times 10^{-18} \exp(-9.161/T_e)$

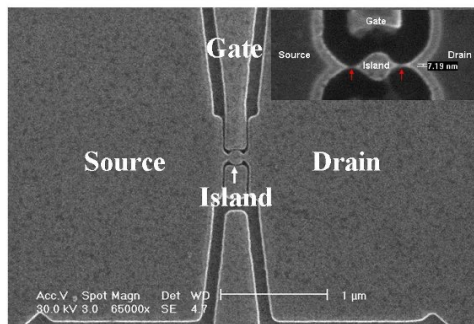
Reactions where we have to "guess"

Charge Exchange Free Electron Forming

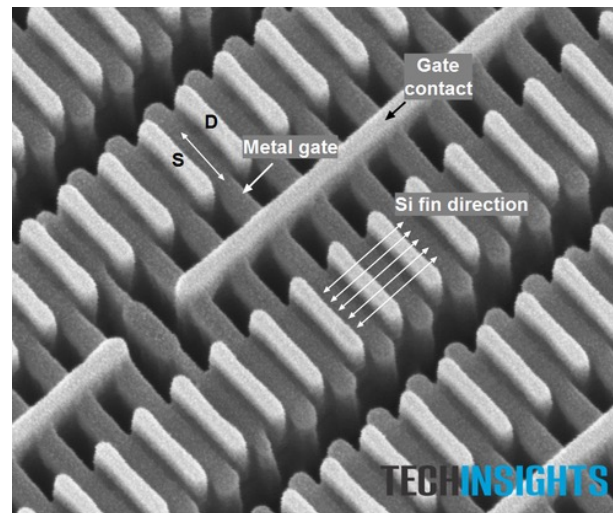
"Boring" Gas Phase Ground State Stuff

Plasma technology has had (and still does) need to keep pace

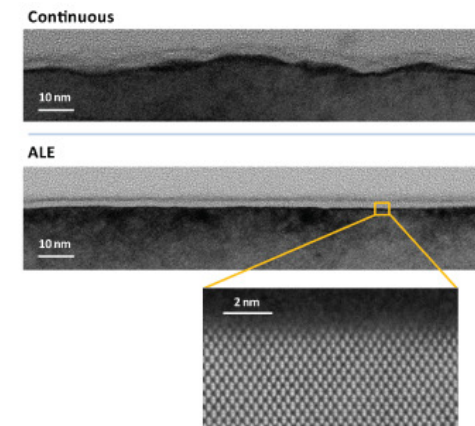
- 1990's – etch rate, etch selectivity, dual damascene
- 2000's – profile shape, aspect ratio, 300mm
- 2010's – aspect ratio, complex material stacks, residual material damage
- 2020's – (one person's opinion at least) – new pathways for anisotropy + advanced chemistry control to maintain anisotropy with minimal device damage down to the atomic scale



Silicon Quantum Dot
 Single electron transistor
 Michael Wang, *Lithography*,
 Intech Press (2010)

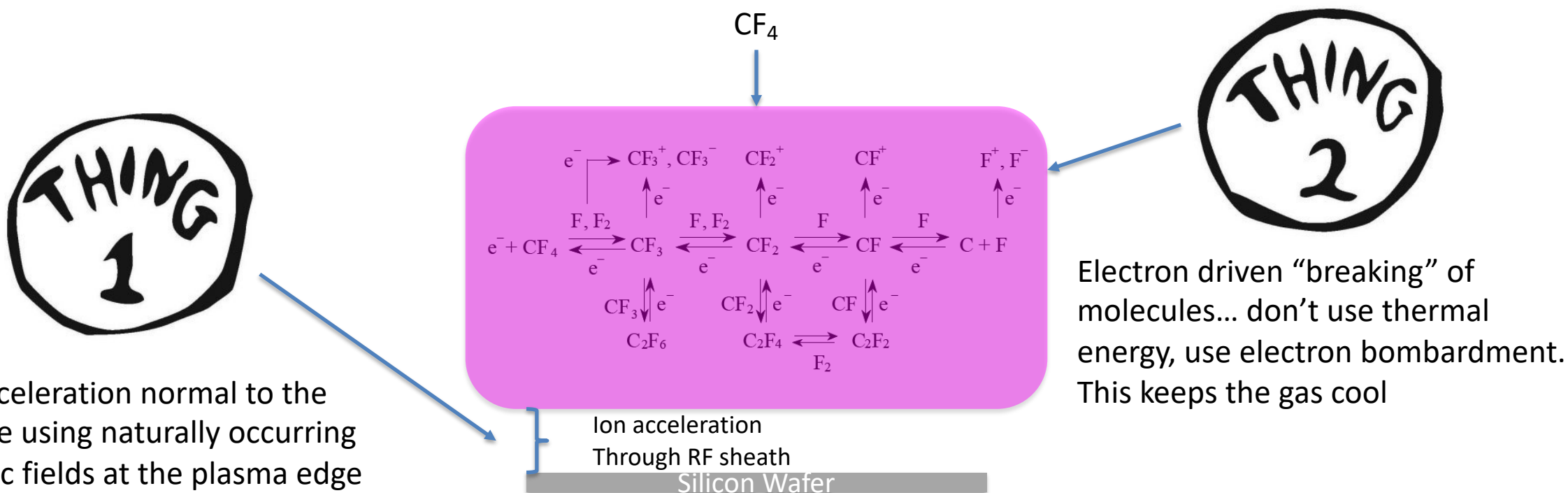


Kevin Gibb, "Samsung's 14 nm LPE
 FinFET Transistors", *EETimes*, 2016



Keren Kanarik et. al., "Moving atomic layer etch
 from lab to fab", *Solid State Technology Magazine*,
 January 2014

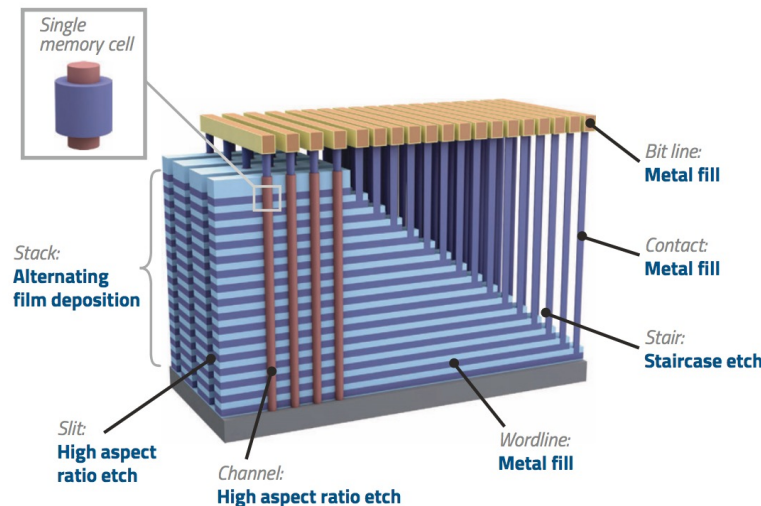
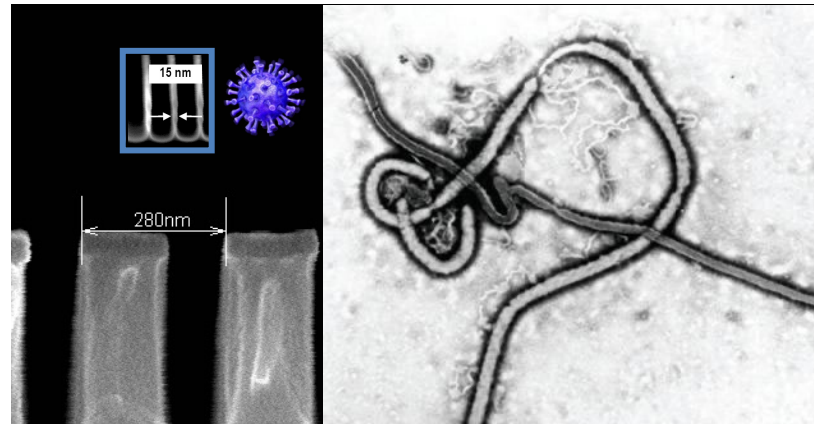
Summary – we need two things to drive device fabrication – ions and reactive low temperature chemistry. Plasmas give us both.



Summary – using plasma technology allows us to combine Thing 1 + Thing 2 to produce the nano-scale devices in electronic equipment today



Ion acceleration normal to the surface using naturally occurring electric fields at the plasma edge



Electron driven “breaking” of molecules... don’t use thermal energy, use electron bombardment. This keeps the gas cool

Acknowledgements

- Countless students, engineers, scientists, and collaborators over the last 25+ years



SAMSUNG

