Basic Mechanisms in Plasma Etching

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Outline

- Brief history of plasma etching, anisotropic vs. isotropic etching, and mechanisms for anisotropy
- Etching product volatility
- Adsorption and reactant sticking coefficients
- Chlorination of Si during chlorine plasma etching
- Chemical etching of Si by F atoms
- Unwanted photo-assisted etching of Si

History of plasmas and plasma etching

- In the early days of integrated-circuit processing, wet-etching was used for pattern transfer.

- In late 1960s – early 1970s, plasma-based pattern transfer replaced wet etching for two reasons:
  1) anisotropic etching for finer feature pattern transfer
  2) eliminate wet chemical waste disposal.

- Early sputtering done with Ar plasmas.

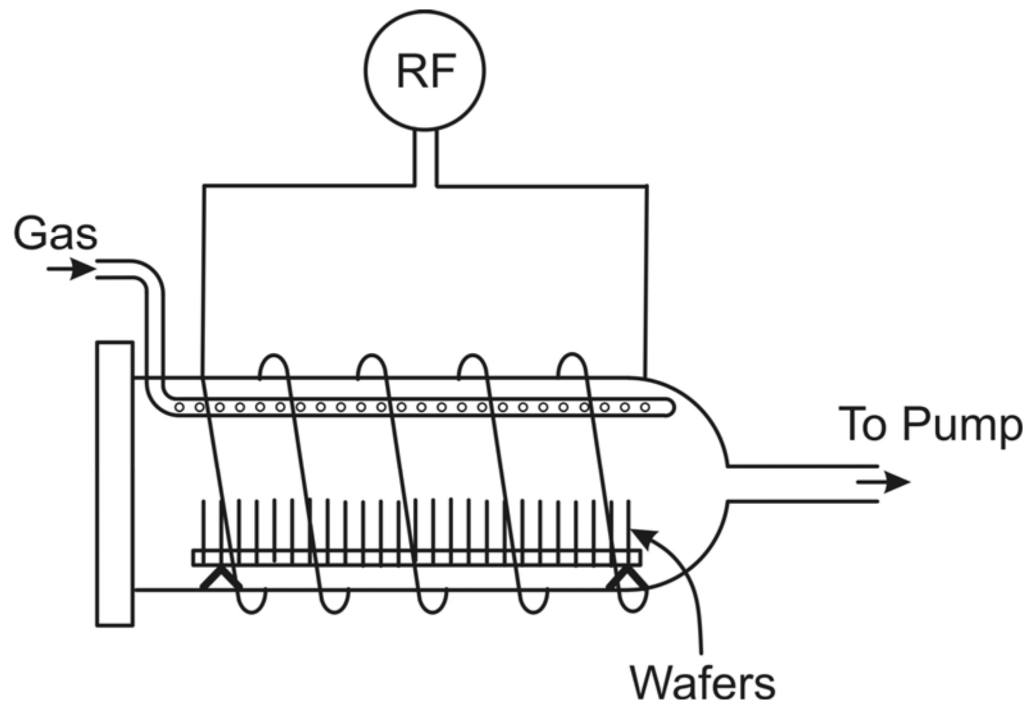
- O_2 plasmas used to strip photoresist.

- Fluorine and chlorine-containing plasmas used to etch Si, SiO_2 and Al.

- Use of additives (e.g. H_2) or alternative gases to CF_4 (C_2F_6, C_3F_8, CHF_3) to increase selectivity of etching of SiO_2 with respect to Si (Heinecke).

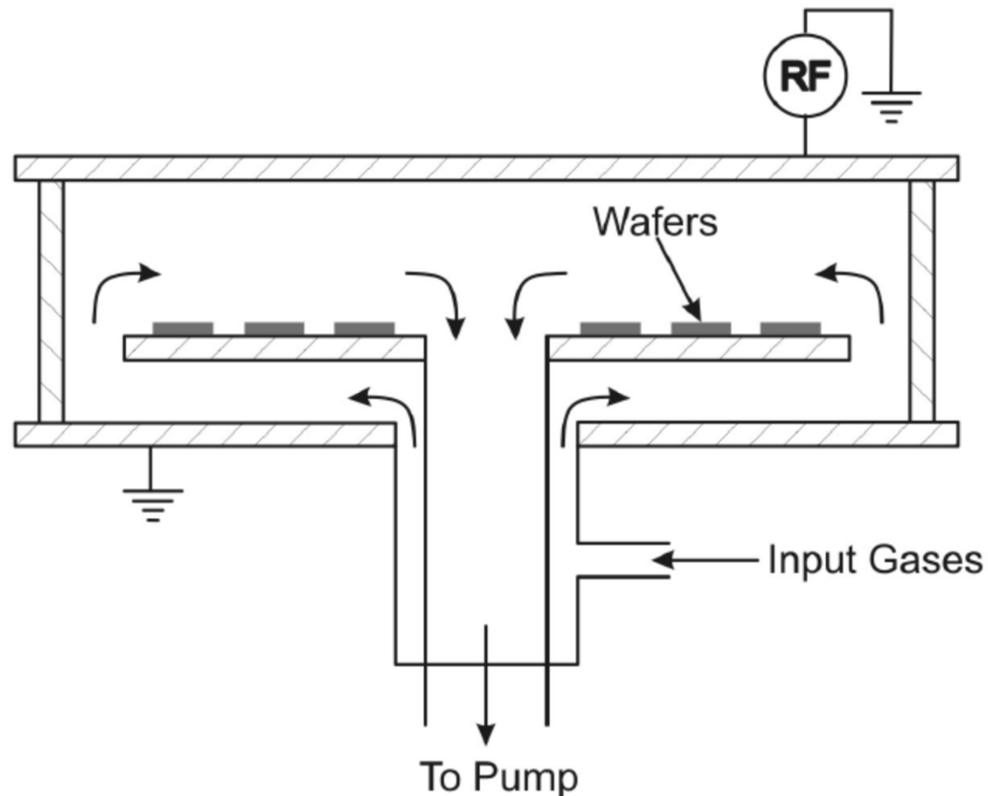
EARLY 1960's BARREL PLASMA ETCHING

- Early plasma reactors were barrel type.
- Wafers were placed in a quartz chamber with external electrodes or coil.
- Adequate for resist stripping. Lacked wafer temperature control. Suffered from etch nonuniformity.
- Low energy ions and high pressure led to isotropic etching.

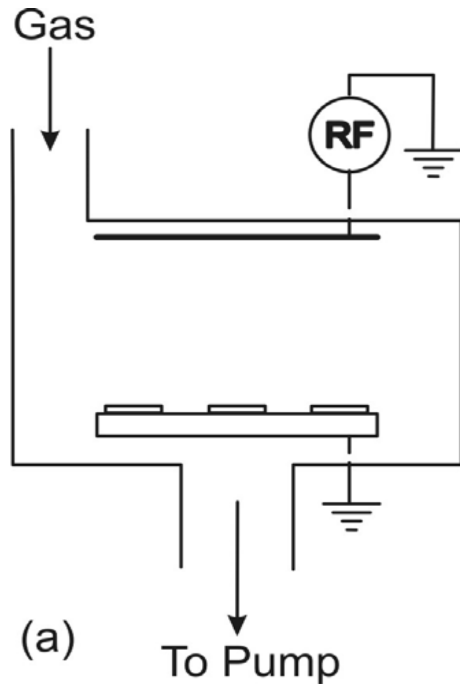


RADIAL FLOW REACTOR (“REINBERG REACTOR”)

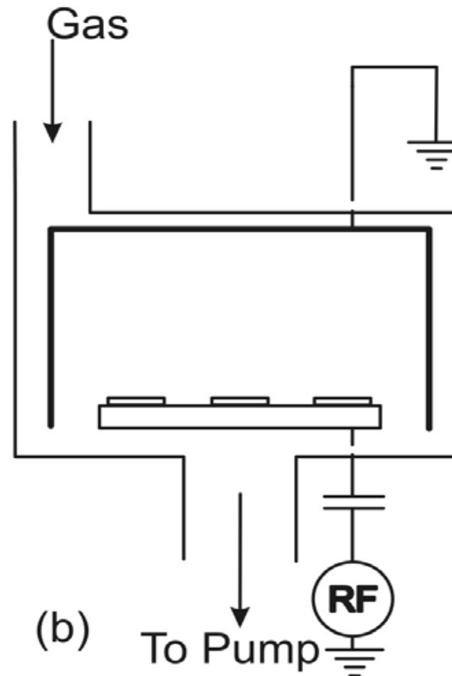
- Inward (radial) flow was thought to compensate for gas consumption.
- Wafers on the grounded electrode; RF applied to opposite electrode.
- Some anisotropy, but still not adequate.



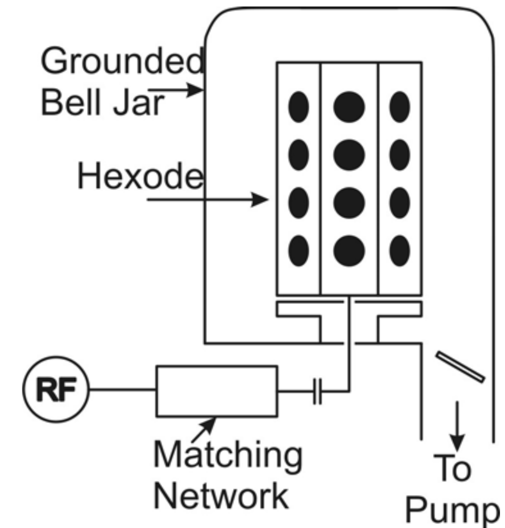
MIGRATION OF WAFERS TO THE SMALLER ELECTRODE



low-energy ion bombardment



high-energy ion bombardment



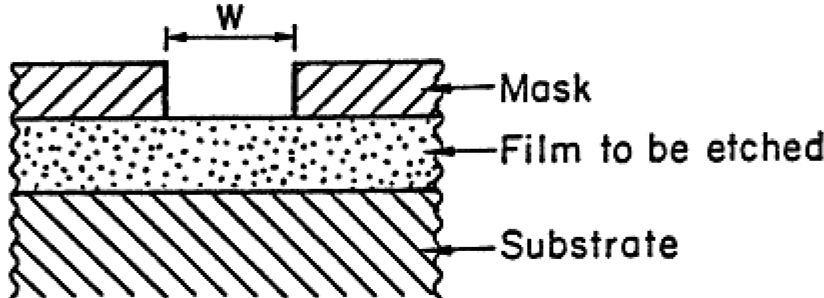
high-energy ion bombardment

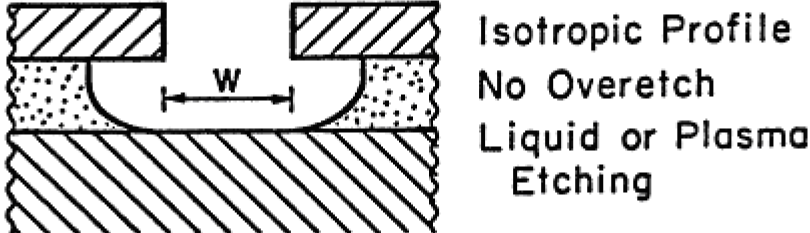
- Motivated by the (incorrect) theory that voltage is inversely proportional to the electrode area ratio to the 4th power.

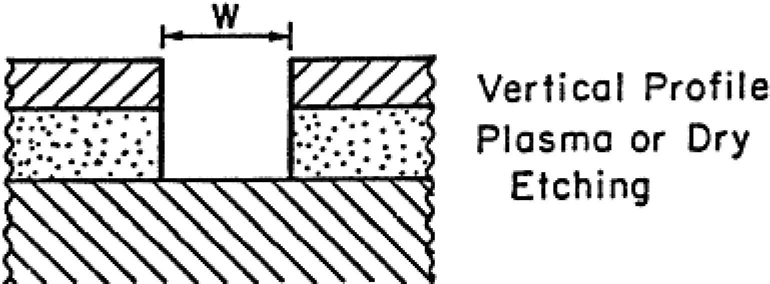
- Actually it scales more like the inverse area ratio to the 1st power. Nonetheless, smaller electrode receives high-energy ion bombardment.

THE NEED FOR ANISOTROPIC PLASMA ETCHING

ISOTROPIC VERSUS ANISOTROPIC ETCHING







Some Basic Considerations in Ion-Assisted Etching

Ion-Neutral Synergy and Ion-Assisted Etching

- **Etching "reactions":**

  Feed gas + plasma → neutral radicals, (+) ions

  radicals + (+) ions + chamber surface → other products

  neutrals (inc. radicals) + (+) ions + wafer → volatile products

- **Characteristics of anisotropic plasma etching:**

  - Perpendicular bombardment of the surface by + ions that are accelerated by a sheath potential

  - Anisotropic etching relies on a *synergy* between ion and neutral reactions on the surface ("*the whole is greater than the sum of its parts*"). First explained in an experiment by Coburn and Winters at IBM Research Laboratories in San Jose, CA. They used ion and molecular beams to simulate a plasma:

Some Basic Considerations in Ion-Assisted Etching

Ion-Neutral Synergy and Ion-Assisted Etching (cont.)

- Coburn and Winters' famous ion and molecular beams experiment:

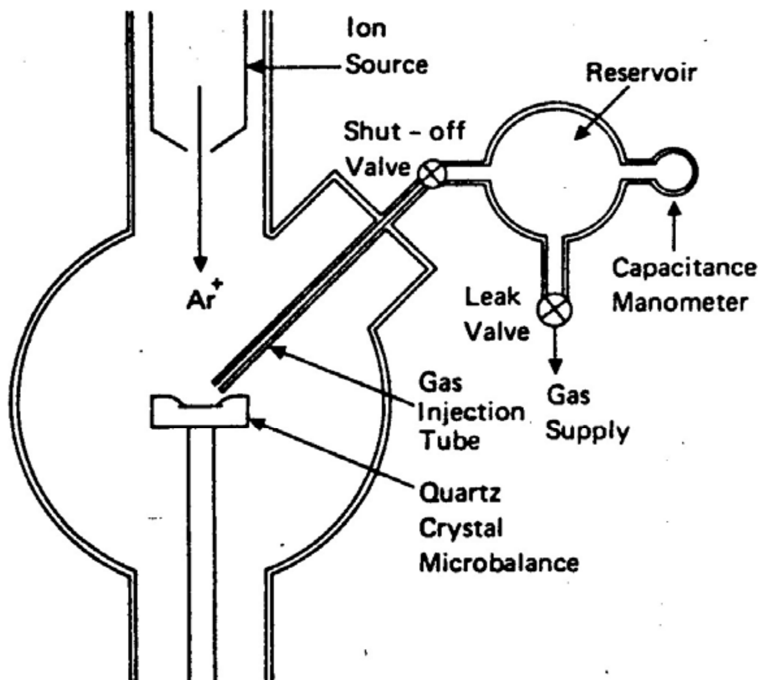


FIG. 1. Schematic diagram of the apparatus used to study ion-assisted gas-surface chemistry. The gas injection tube is 1.6 mm inside diameter and is about 3 mm from the quartz crystal microbalance. The gas flow is determined from the rate of pressure increase in the reservoir when the shut-off valve is closed.

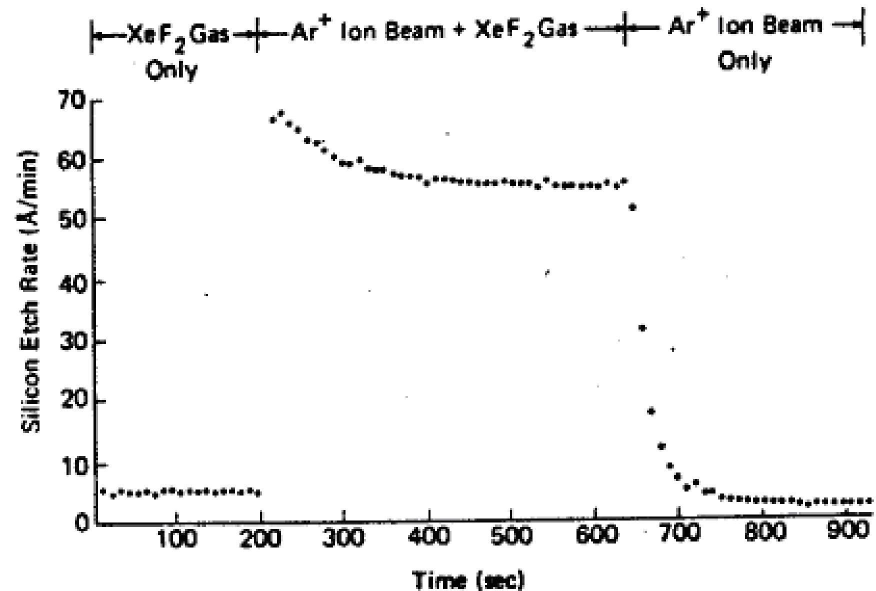
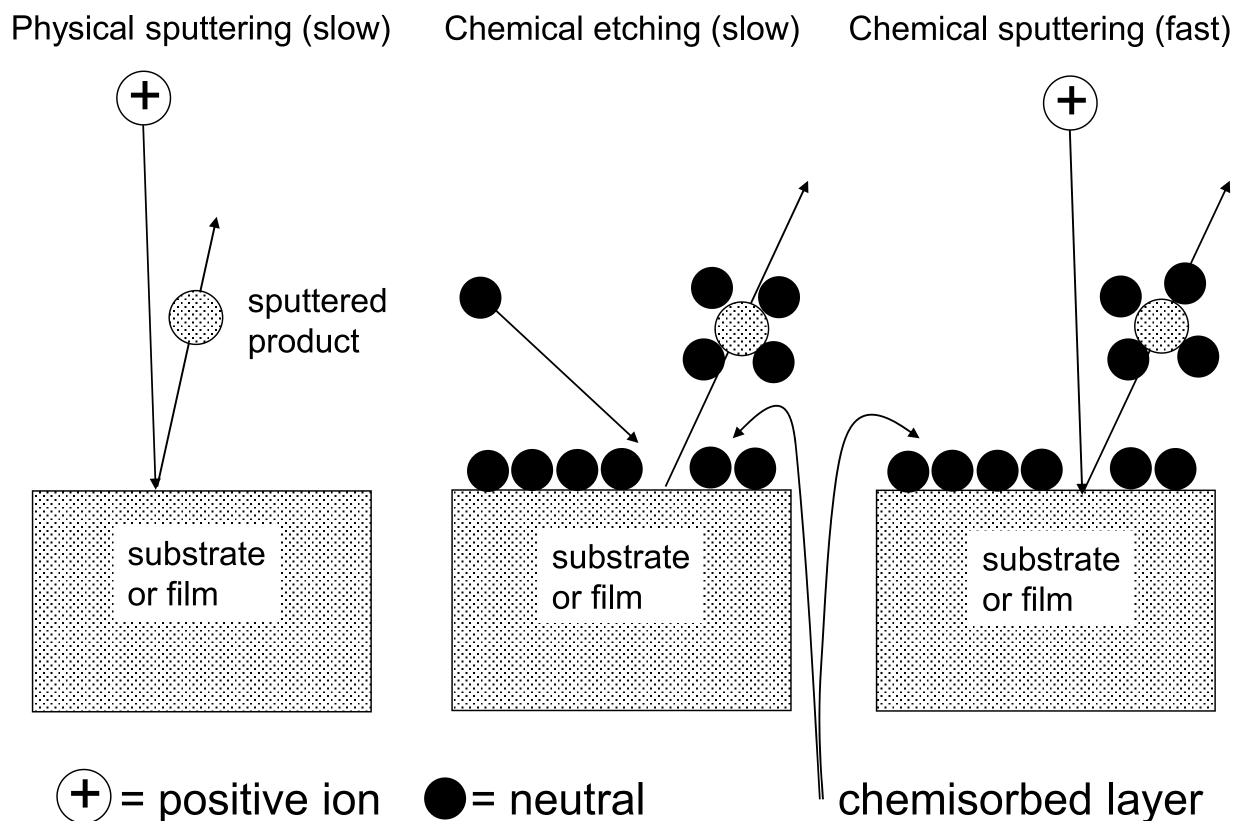


FIG. 2. Ion-assisted gas-surface chemistry using Ar^+ and XeF_2 on silicon (volatile reaction product). Ar^+ energy = 450 eV, Ar^+ current = 0 ($t < 200$ sec), Ar^+ current = 2.5 μA ($t > 200$ sec), XeF_2 flow = 2×10^{15} mol/sec ($t < 660$ sec), and XeF_2 flow = 0 ($t > 660$ sec). (The Ar^+ current density and the XeF_2 flux are not uniform over the Si surface. The effective area for the Ar^+ current and the XeF_2 flux are estimated at 0.1 and 0.3 cm^2, respectively.)

Etching Mechanism 1:

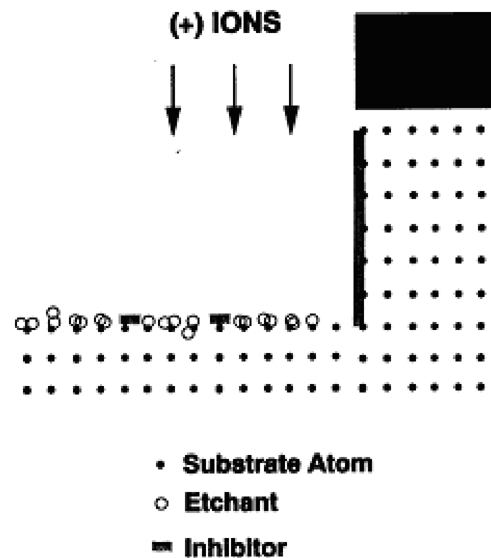


- **Good example of chemical sputtering: Si etching in a Cl_2 plasma.**

Etching Mechanism 2: Sidewall Inhibitor

• Isotropic chemical etching is sometimes very fast. This process can be slowed or stopped by adding an "inhibitor" to the plasma gas.

• Inhibitor coats vertical sidewall but is sputtered away on horizontal surfaces.

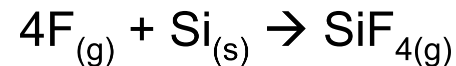


• Good examples of sidewall inhibitor: 1) etching of photoresist-masked Al in a Cl_2/BCl_3 plasma; 2) Bosch process for MEMS etching in SF_6 and C_4F_8 pulsed gas plasmas.

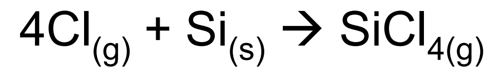
THE IMPORTANCE OF VOLATILE PRODUCTS

- Plasma etching is the gasification of a solid by reactive species that are formed in the plasma.

- For example, fluorine and chlorine atoms are known to convert solid silicon into gaseous SiF_4 and $SiCl_4$. The overall reactions are:



$$4F_{(g)} + Si_{(s)} \rightarrow SiF_{4(g)}$$



$$4Cl_{(g)} + Si_{(s)} \rightarrow SiCl_{4(g)}$$

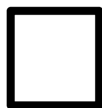
- Ion bombardment also accelerates these reactions.

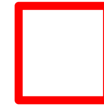
Periodic Table of the Elements

1 1IA 11A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 H Hydrogen 1.0079																	2 He Helium 4.00260
3 Li Lithium 6.941	4 Be Beryllium 9.01218											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.998403	10 Ne Neon 20.1797
11 Na Sodium 22.989768	12 Mg Magnesium 24.305											13 Al Aluminum 26.981539	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.95591	22 Ti Titanium 47.88	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938	26 Fe Iron 55.847	27 Co Cobalt 58.9332	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.732	32 Ge Germanium 72.64	33 As Arsenic 74.92159	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium 98.9072	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.9055	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.90447	54 Xe Xenon 131.29
55 Cs Cesium 132.90543	56 Ba Barium 137.327	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.9665	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98037	84 Po Polonium [208.9824]	85 At Astatine 209.9871	86 Rn Radon 222.0176
87 Fr Francium 223.0197	88 Ra Radium 226.0254	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown

Series															
Lanthanide Series	57 La Lanthanum 138.9055	58 Ce Cerium 140.115	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.24	61 Pm Promethium 144.9127	62 Sm Samarium 150.36	63 Eu Europium 151.9655	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
Actinide Series	89 Ac Actinium 227.0278	90 Th Thorium 232.0381	91 Pa Protactinium 231.03588	92 U Uranium 238.0289	93 Np Neptunium 237.0482	94 Pu Plutonium 244.0642	95 Am Americium 243.0614	96 Cm Curium 247.0703	97 Bk Berkelium 247.0703	98 Cf Californium 251.0796	99 Es Einsteinium [254]	100 Fm Fermium 257.0951	101 Md Mendelevium 258.1	102 No Nobelium 259.1009	103 Lr Lawrencium [262]

Alkali Metals | Alkaline Earths | Transition Metals | Basic Metals | Semi-Metals | Nonmetals | Halogens | Noble Gases | Lanthanides | Actinides

 **Solid elements to be etched**

 **gaseous etchant elements**

Volatile the etching products in halogen, carbon, hydrogen, and oxygen-containing plasmas are SiF_4, SiF_2, $SiCl_4$, $SiCl_2$, $SiBr_4$, $SiBr_xH_y$, $SiCl_xBr_yH_z$, $SiOF_2$, CO, CO_2, O_2, COF_2, metal halides and metal oxy-halides.

Some Basic Considerations in Etching

Vaporization of Products

- For a compound to be sufficiently volatile, its evaporation rate should be much higher than the desired etching rate.

- The maximum evaporation rate is computed by the principle of detailed balance: at equilibrium, the forward and reverse rates of every elementary process are equal.

- Consequently, for a gaseous species at a number density, *n*, in equilibrium with its liquid or solid state in a closed system, its evaporation rate equals its impingement rate on the solid or liquid.

- The impingement rate or flux (molecules-cm^{2}s^{-1}) of species onto a surface is

$$f_i = \frac{nv}{4}$$

Some Basic Considerations in Etching
Vaporization of Products (cont.)

- The thermal speed, *v* (in cm/s), is given by

$$v = \left(\frac{8kT}{\pi m}\right)^{1/2}$$

where *k* is the Boltzman constant (8.314×10^{7} erg K^{-1}mole^{-1}), *T* is the temperature in Kelvin, and *m* is the mass in grams/mole.

- For an ideal gas at pressure *p* (in dyne-cm^{-2} [1 dyne-cm^{-2} = 0.1 Pa = 7.502×10^{-5} Torr]), the impingement rate is

$$f_i = \frac{p}{\sqrt{2\pi mkT}}$$

- The equilibrium vapor pressure, p_V, is given by the Clausias-Claperon equation:

$$p_V = p_0 \exp\left(\frac{-\Delta H}{RT}\right)$$

Some Basic Considerations in Etching

Vaporization of Products (cont.)

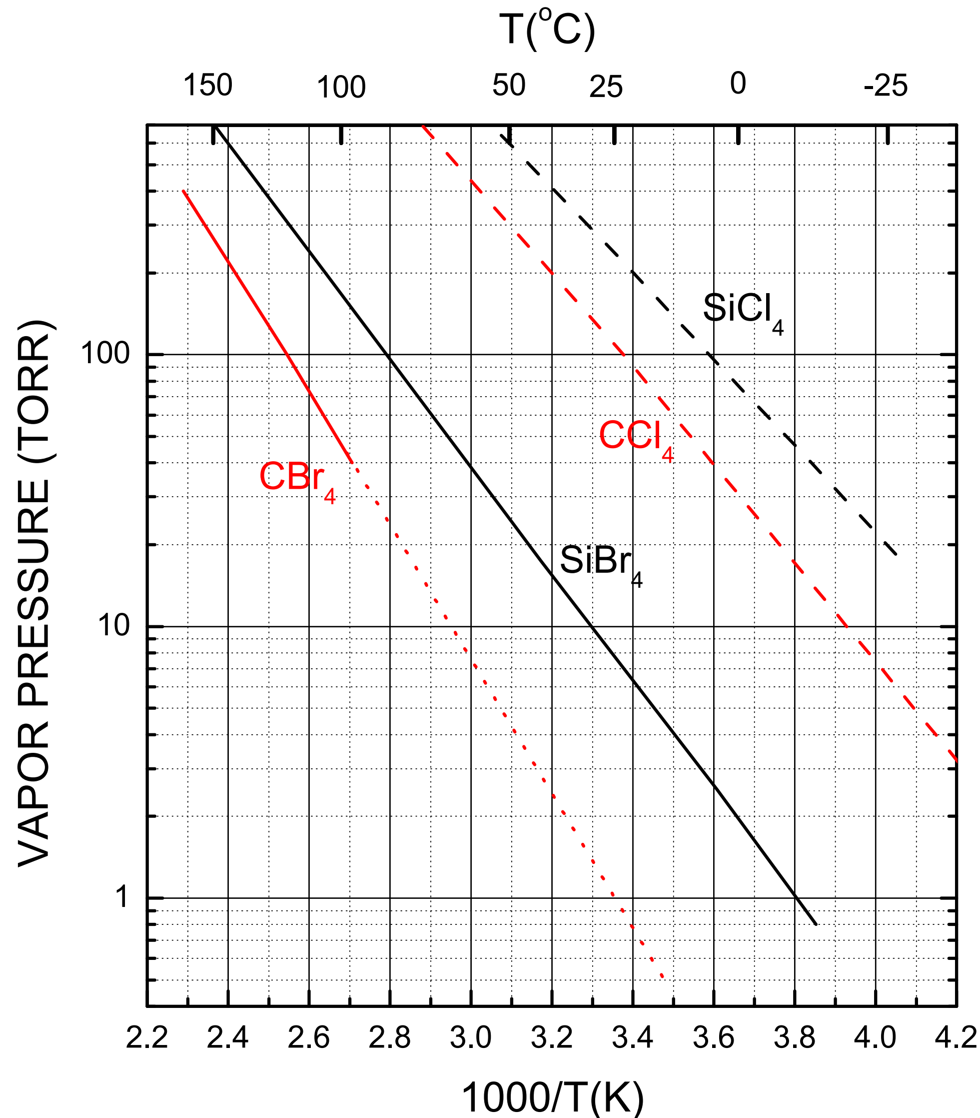
where ΔH is the heat of vaporization and p_0 is a constant of integration. Consequently, at equilibrium, the evaporation rate (equals the impingement rate) is given by

$$f_e = f_i = \frac{p_V}{\sqrt{2\pi mkT}}$$

- **NOTE: The evaporation rate is given by the right side of this equation, regardless if the system is closed or open and far from equilibrium, as it always in in plasma etching.**

Some Basic Considerations in Etching

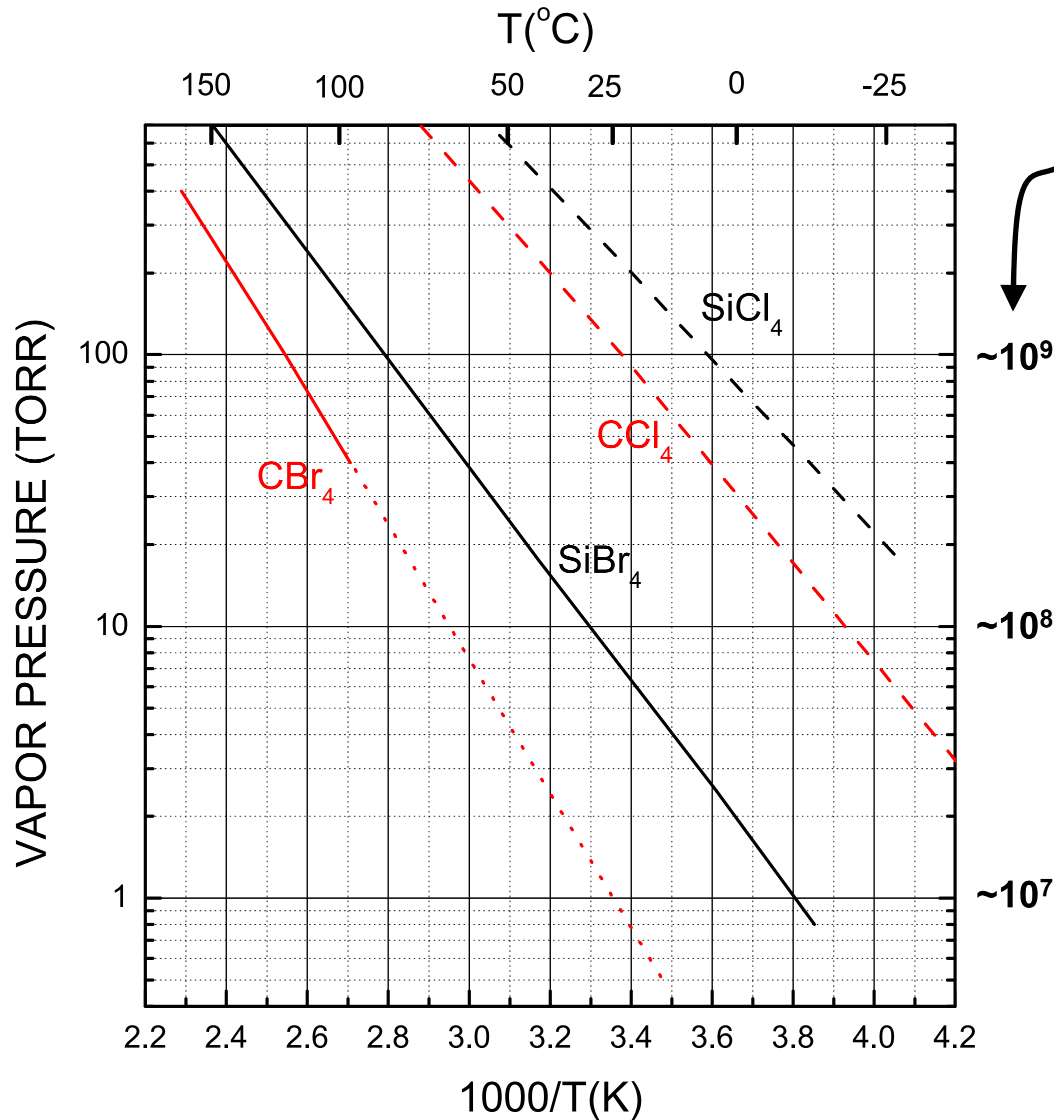
Vaporization of Products (cont.)



- Equilibrium vapor pressures of Si and C halides.
- (SiF_4 and CF_4 are gases).
- Note the much lower vapor pressures of the Br compounds relative to Cl (and F) products.
- Does this explain slower etching rates for Br? No.

Some Basic Considerations in Etching

Vaporization of Products (cont.)



Etching rates (Å/min) if limited by product vaporization rate.

- ∴ Si and C etching in Cl or Br-containing plasmas not limited by vaporization of tetrahalide compounds.

Some Basic Considerations in Etching

Product Desorption Rates

- For a species to be present on the surface during etching, it must be strongly adsorbed. The rate of thermal desorption (s^{-1}) is given by

$$k_d = \upsilon_0 \exp(-E_a / RT)$$

- ν_0 is the pre-exponential or so-called attempt frequency and E_a is the activation energy for desorption (i.e. binding energy) of the adsorbate.

- ν_0 is often set equal to a typical vibrational frequency of ~$10^{13}s^{-1}$, but in fact $\nu_0 = kT/h(q_{ts}/q_r)$, where q_{ts} and q_r are partition functions of the transition state for desorption and the reactant state.

- ν_0 can vary from typically 10^8 to 10^{15} s^{-1}.

- E_a can also span a wide range of values, reflecting the complex nature of the surface layer and the multitude of bonding configurations.

Some Basic Considerations in Etching

Product Desorption Rates (cont.)

- Using $\nu_0 = 10^{13} s^{-1}$ and above eq. for k_d, it follows that for a species to have a lifetime ($1/k_d$) ~0.1s on the surface, comparable to the time required to etch 1 monolayer, must have a binding energy, E_a = 16 kcal/mole (0.69 eV) at room temperature.

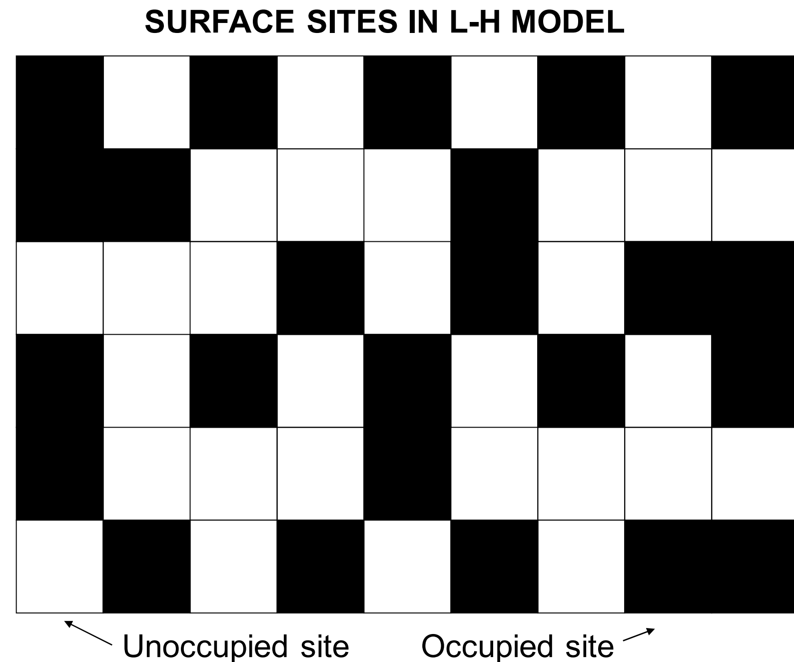
- E_a = 16 kcal/mole exceeds physisorption energies for most adsorbate-substrate combinations. Products like $SiBr_4$ should be much more weakly bound and therefore desorb nearly instantaneously after being formed.

- E_a = 16 kcal/mole is less than most chemical bonds, consequently any chemisorbed species will likely live indefinitely on the surface.

- Therefore, surfaces are covered with chemisorbed species during and after etching.

Some Basic Considerations in Etching

Adsorption and Etching by Neutrals



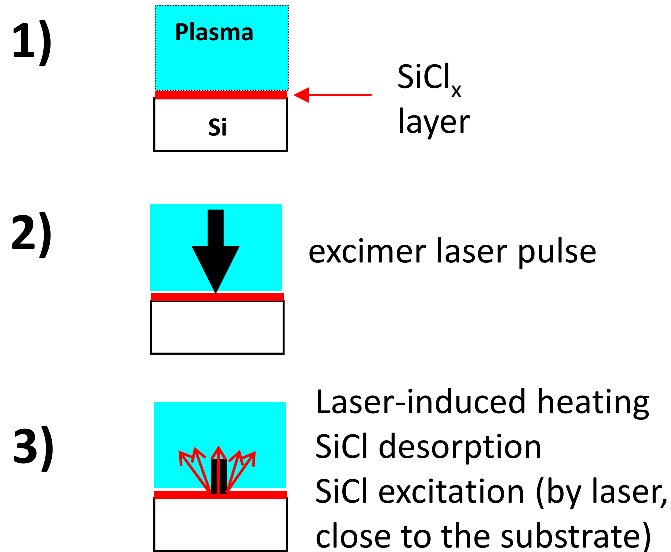
- A sticking coefficient can be defined by the Langmuir-Hinshelwood (L-H) adsorption model.

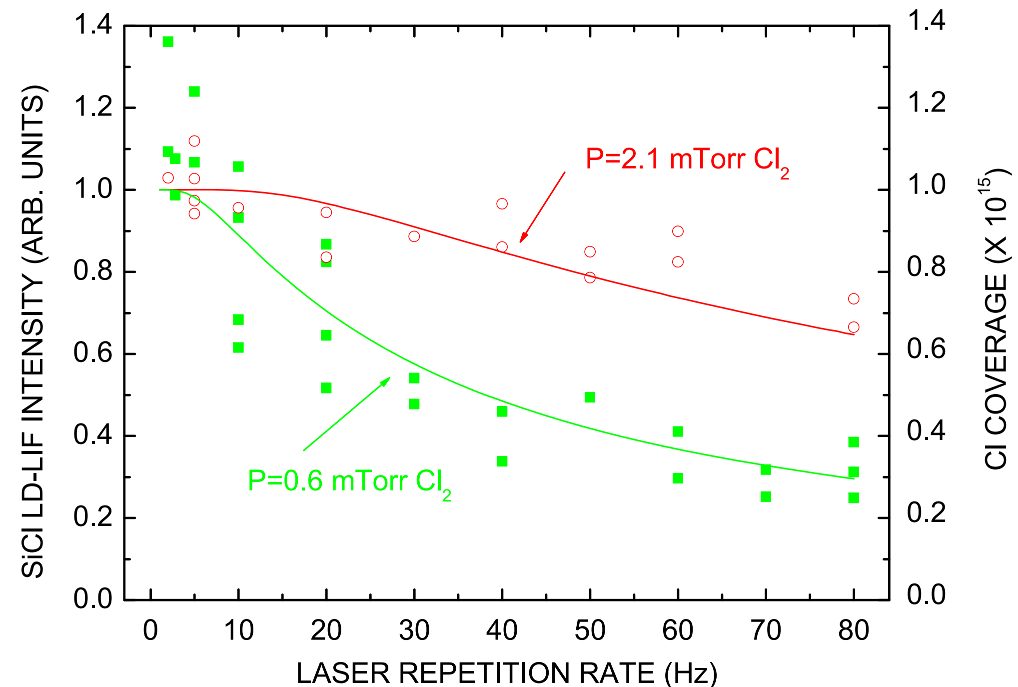
- θ = relative density of adsorption sites ($0 < \theta < 1$). The probability for adsorption is $k_{ads} = S(1-\theta)$ where *S* is the sticking coefficient (or sticking probability) at an unoccupied site.

- When all sites are occupied, the probability for adsorption is zero. Most etching processes operate near this limit.

- On atomically rough surfaces that are present during etching, the adsorption and diffusion processes are more complicated, with a range of differing adsorption sites and rates.

Cl Uptake on Si (100) in a Cl_2 plasma

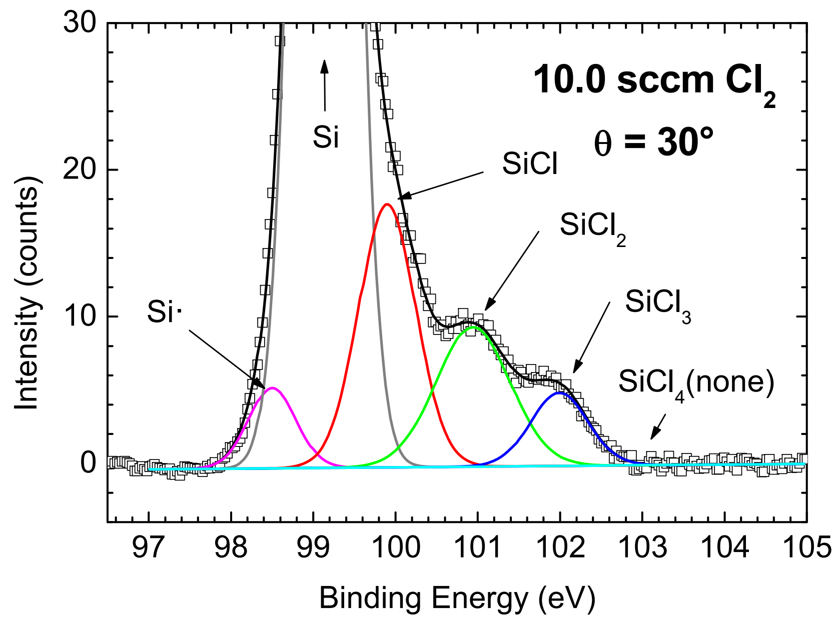


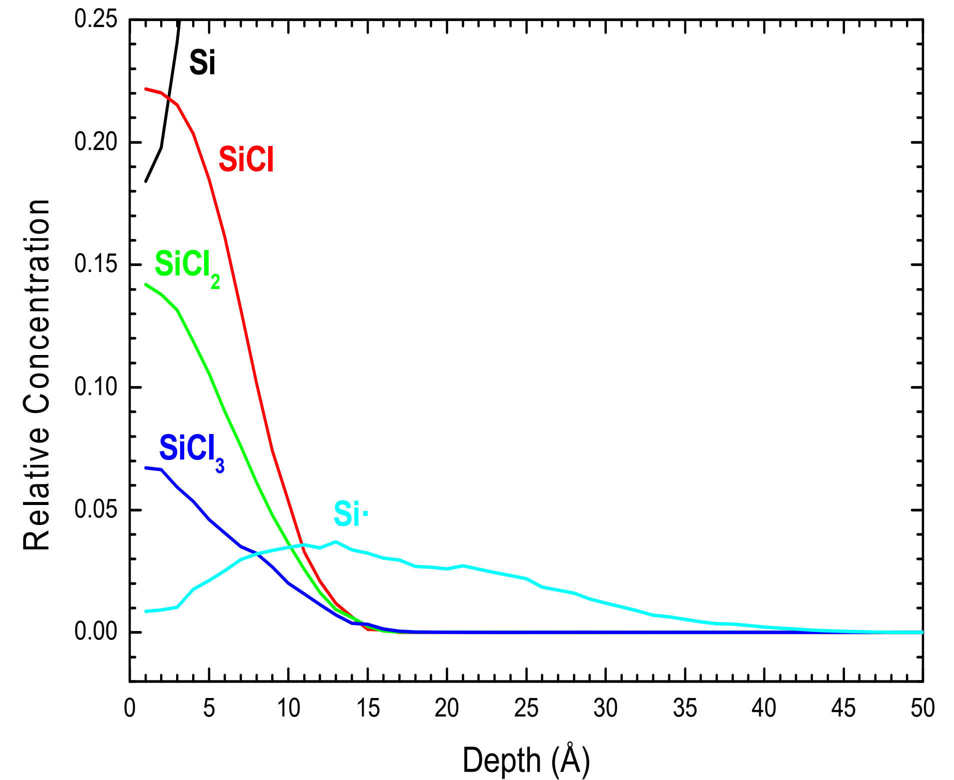


- A simple Langmuir-Hinshelwood (L-H) model was fit to the measurements.

- The model reproduces that trends at both pressures with a single sticking coefficient times flux, where the chlorinating species could be Cl, Cl_2, Cl^+ and Cl_2^+. The chlorination rate constant is $8 \times 10^4 s^{-1} Torr^{-1}$ for a plasma with ~10% dissociation of Cl_2 and an ion density of $\sim 5 \times 10^{10} cm^{-3}$.

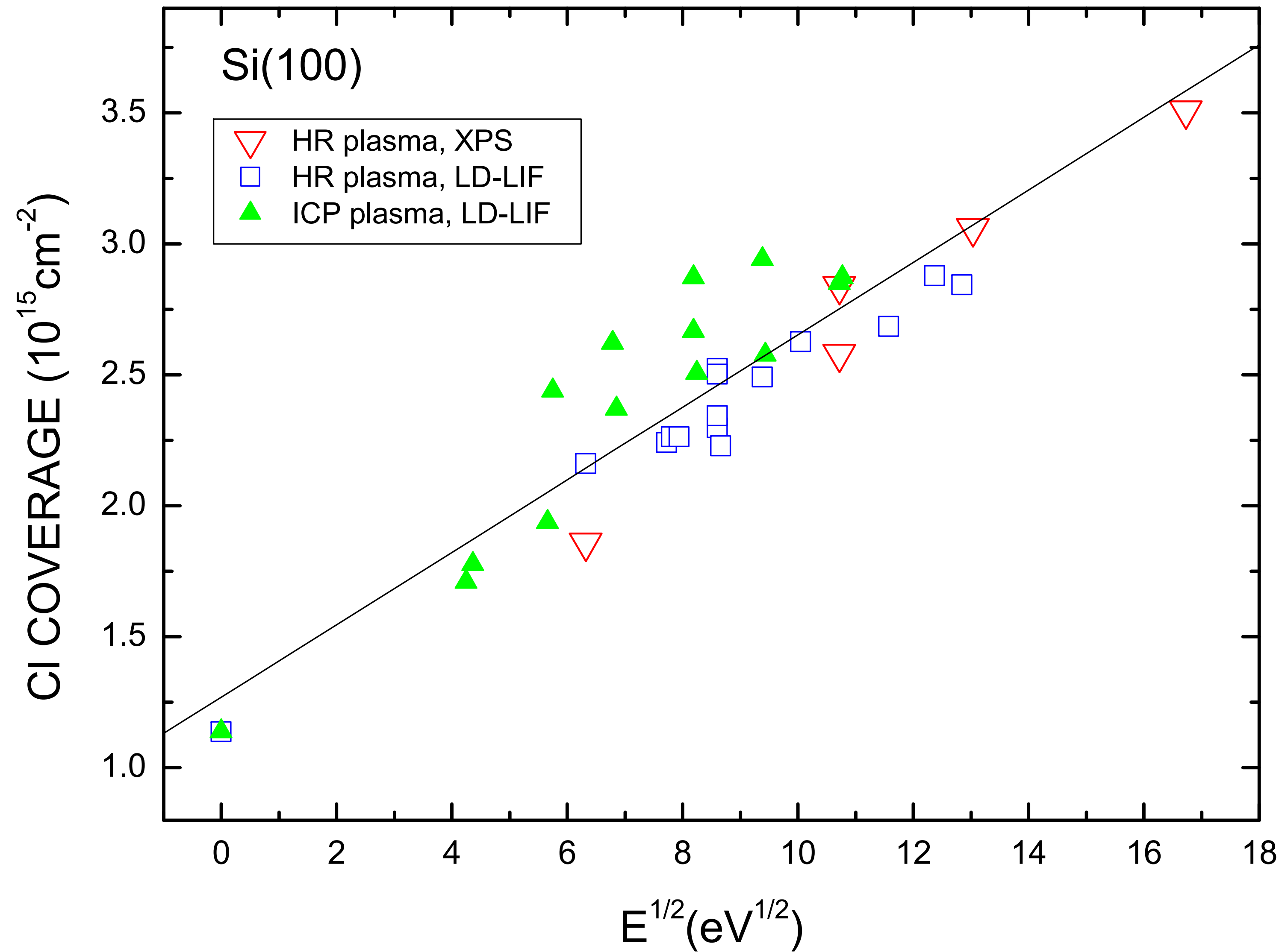
Cl Uptake on Si (100) in a Cl_2 plasma





- $SiCl_x$ ~ 16 Å
- $SiCl > SiCl_2 > SiCl_3 > SiCl_3O$ depth and concentration
- Si·deep into layer

Cl Uptake on Si (100) in a Cl_2 plasma: Dependence on Ion Energy



Cl Uptake on Si (100) in a Cl_2 plasma: Dependence on Ion Energy

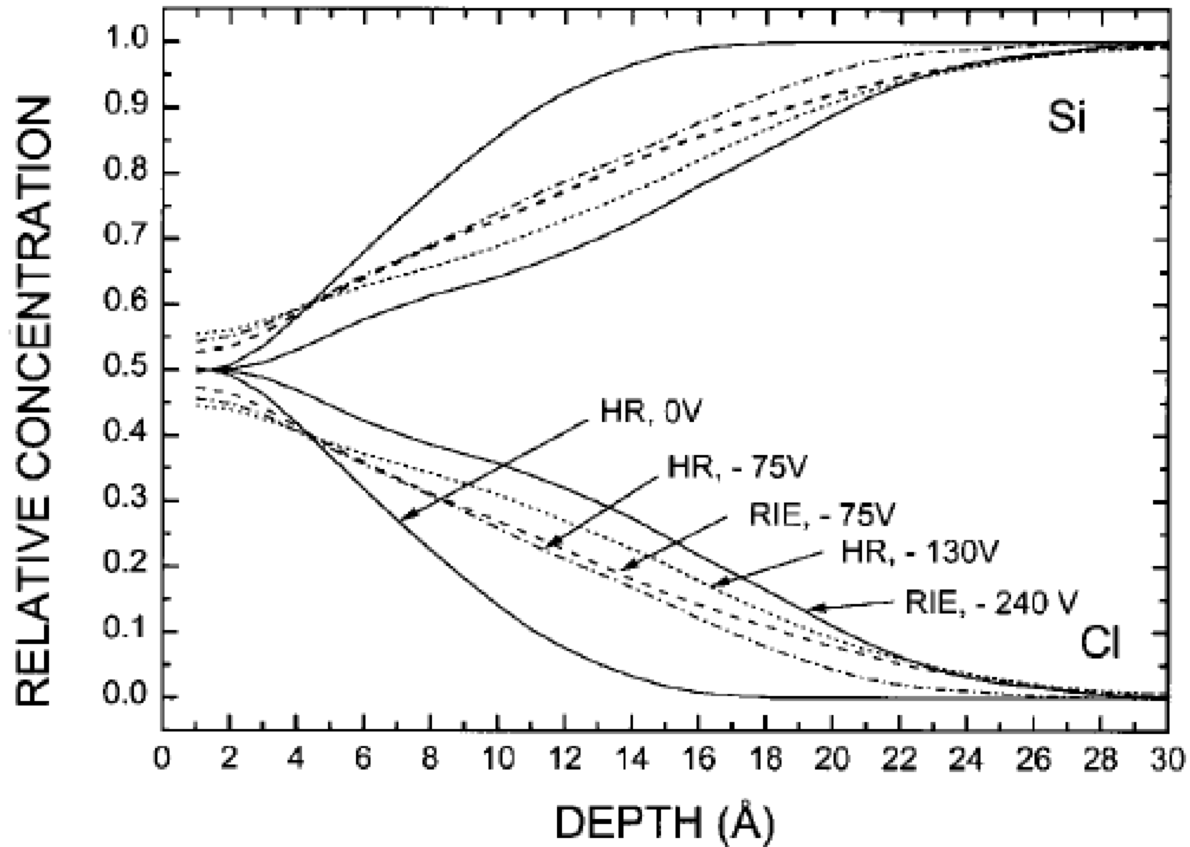


FIG. 11. Depth profiles of Cl and total Si concentrations for Si(100) samples after etching for 30 s in Cl_2 plasmas under different processing conditions, determined from an inversion of take-off angle dependent XPS data in Fig. 3.

Some Basic Considerations in Etching

Adsorption and Etching by Neutrals (cont.)

- Some materials (e.g. Si) will be etched by neutrals (e.g. F-atoms) in the absence of ion bombardment. **This reaction is mainly responsible for deep Si etching in SF_6 plasmas.**

- Define a reaction coefficient for etching, $\varepsilon_{X(S)}$, as the probability that an atomic or molecular material, S, will be converted into a volatile products per impinging neutral, X (in the absence of ion bombardment or other sources of energetic particles),

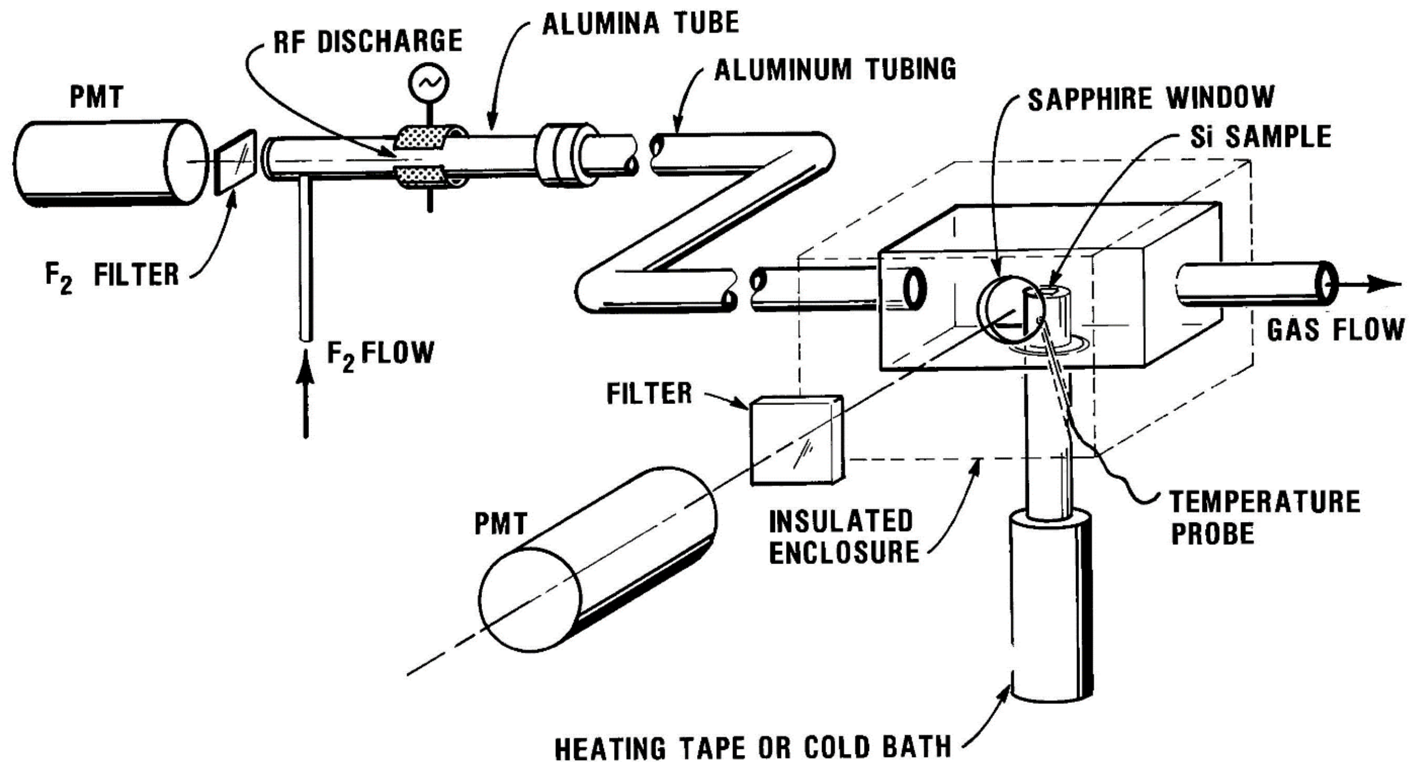
$$\varepsilon_{X(S)} = \frac{N_A \, \rho_S \, R_{X(S)}}{M_S \, (n_X v_X / 4)}$$

$R_{X(S)}$ = etching rate, N_A = Avogadro's number, r_S and M_S are density and mass of the substrate. (e.g. if 1000 impinging F atoms per area per time leads to 1 Si atom being etched, $\varepsilon_{X(S)} = 0.001$.

- If $\varepsilon_{X(S)} << S$ *(S = sticking coefficient defined 2 slides back)*, then $\theta \approx 1$.

One Way to Measure $\varepsilon_{X(S)}$: Downstream Reactor

D.L. Flamm, V.M. Donnelly, and J.A. Mucha, *The reaction of fluorine atoms with silicon.* J. Appl. Phys, 1981. **52**: p. 3633.



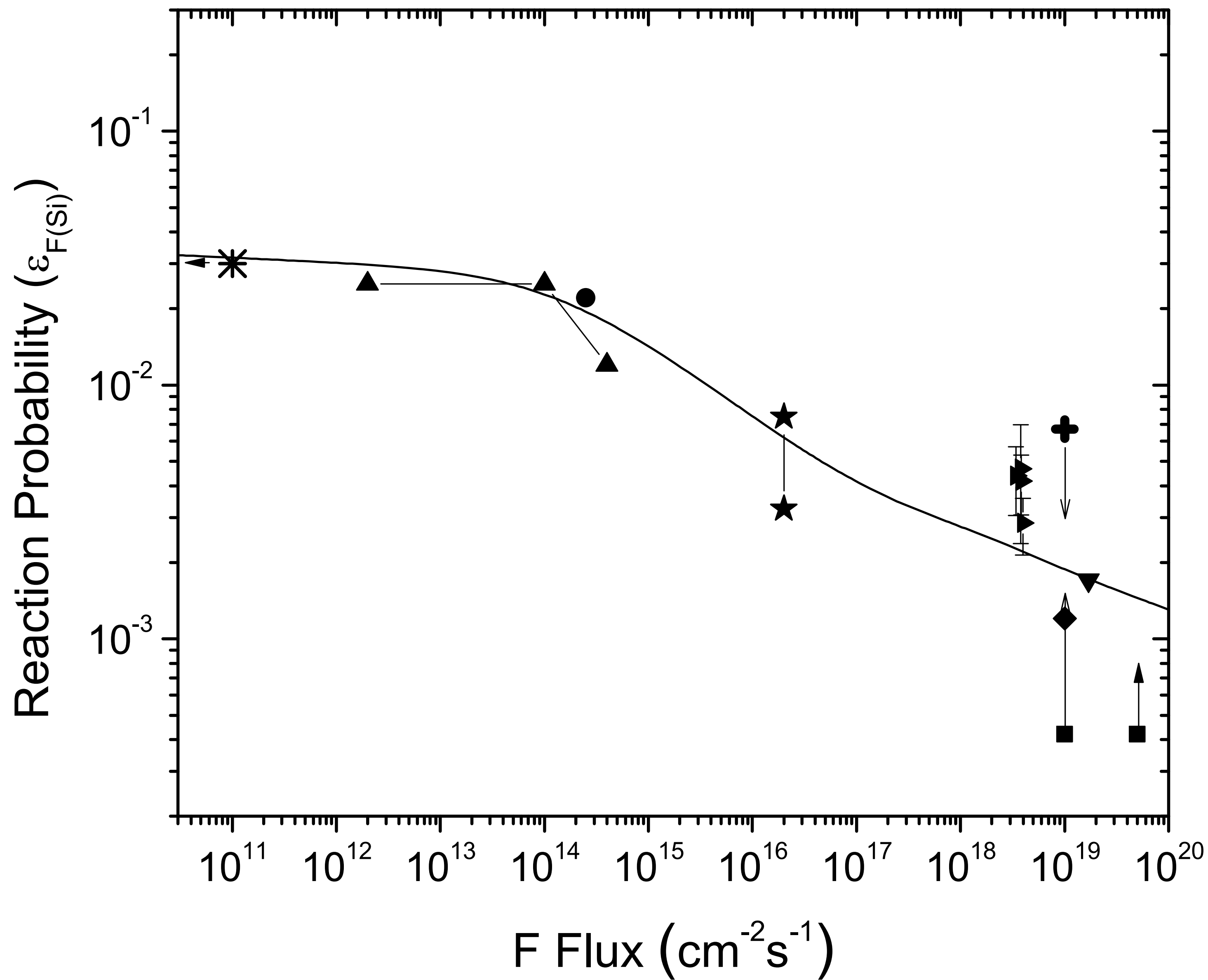
- Eliminate ion bombardment
- Measure absolute F number density by chemical titration.

Summary of Published Reaction Probabilities for F +Si

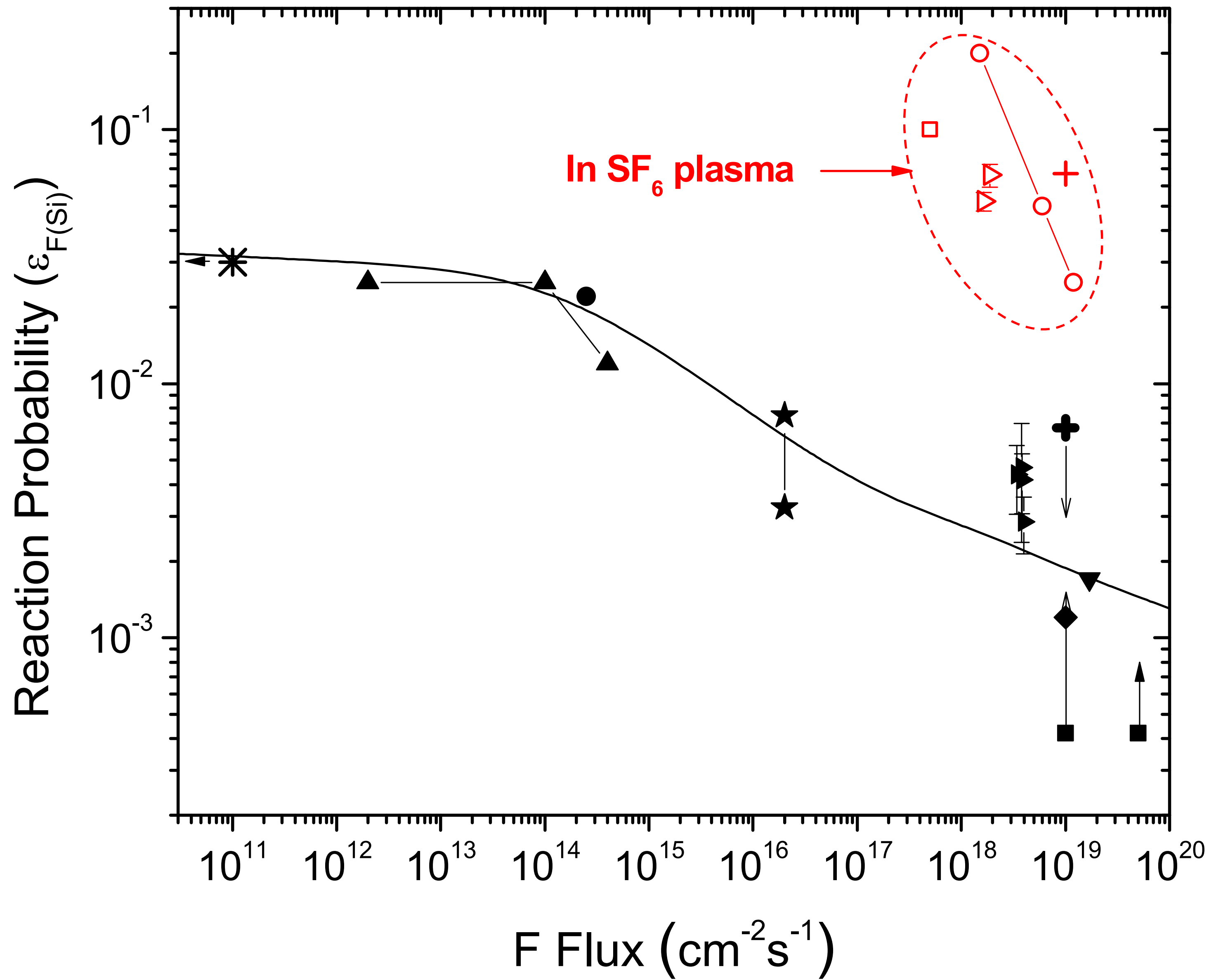
- Reported values (when corrected) range from 0.00042 to 0.1!
- How to explain this 240-fold discrepancy?

References	$\varepsilon_{F(Si)}$
Flamm *et al.* (Ref. 11)	0.00042
Vasile and Stevie (Ref. 14)	0.022
Ninomiya *et al.* (Ref. 31)	0.025
	0.012
Mogab *et al.* (Ref. 6)	~0.0017
Lee and Chen (Ref. 39)	0.0012
Winters and Plumb	<0.01
(Refs. 16 and 18)	0.00325–0.0075
Hays *et al.* (Ref. 42)	<0.0067
Hays *et al.* (Ref. 42)	~0.067
Humbird and Graves (Ref. 18)	0.03
Herrick, *et al.* (Ref. 40)	0.1
Aydil and coworkers (Ref. 41)	0.2
	0.05
	0.025
Ma *et al.* (Ref. 46)	0.00223
	0.00319
	0.00234
	0.00319
Ma *et al.* (Ref. 46)	0.0617
	0.0476

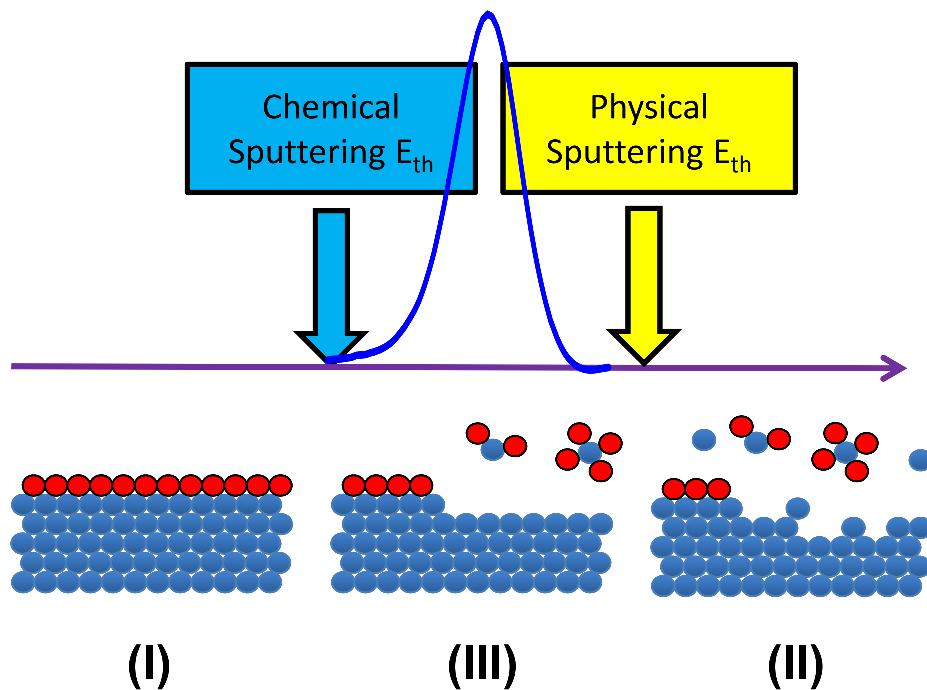
F + Si Reaction Probability Exhibits Strong Flux Dependence



F + Si Reaction Probability Much Higher in SF_6 Plasmas



Motivation : Precise Control of IED for ALE



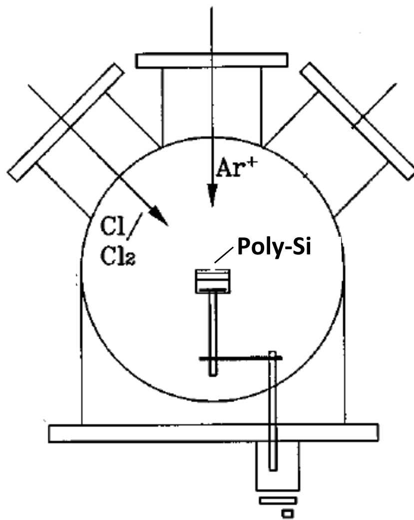
(I) Low energy ions : No reaction occurs except for pure chemical etching, if any.

(II) High energy ions: chemical sputtering, sub-surface ion penetration, physical sputtering → not well-controlled etching, substrate damage.

(III) Medium energy ions: Only chemical sputtering. More confined to surface. Etching slows or stops when adsorbed etchant reacts away. → minimum damage, layer-by-layer etching.

- Layer-by-layer etching, high selectivity, and no substrate damage are/will be critical requirements. To achieve these, one needs to control the IED.
    - Accurate control of peak ion energy.
    - Narrow width of IED.
    - Work with medium energy ions (region III).

Ion Energy Dependence of Si Etching in Chlorine-Containing Plasmas

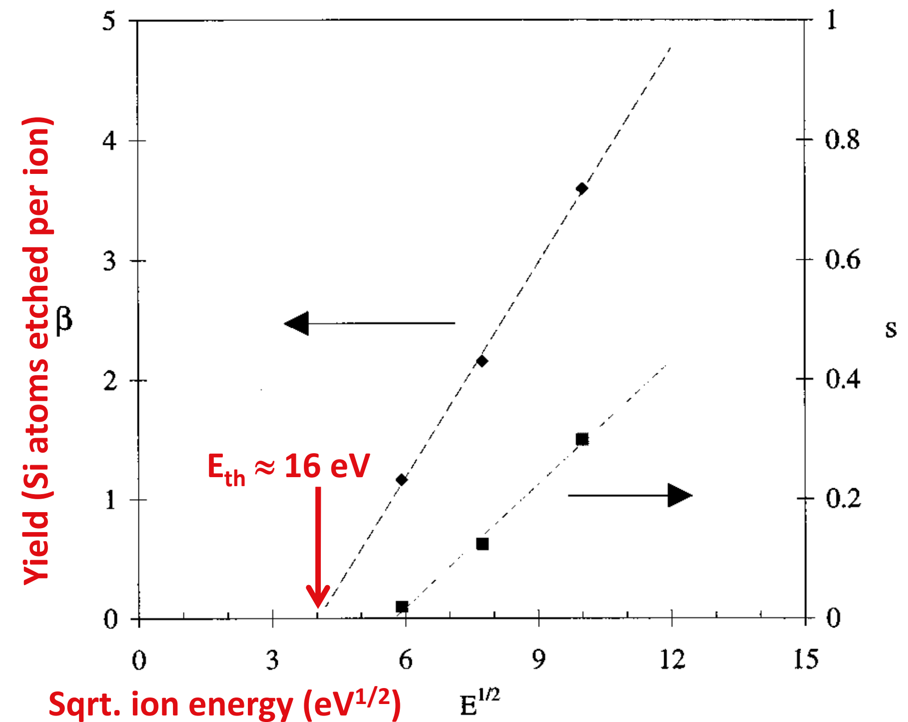


Characteristics of polycrystalline Si etching with Cl and Ar^+ beams in high vacuum:

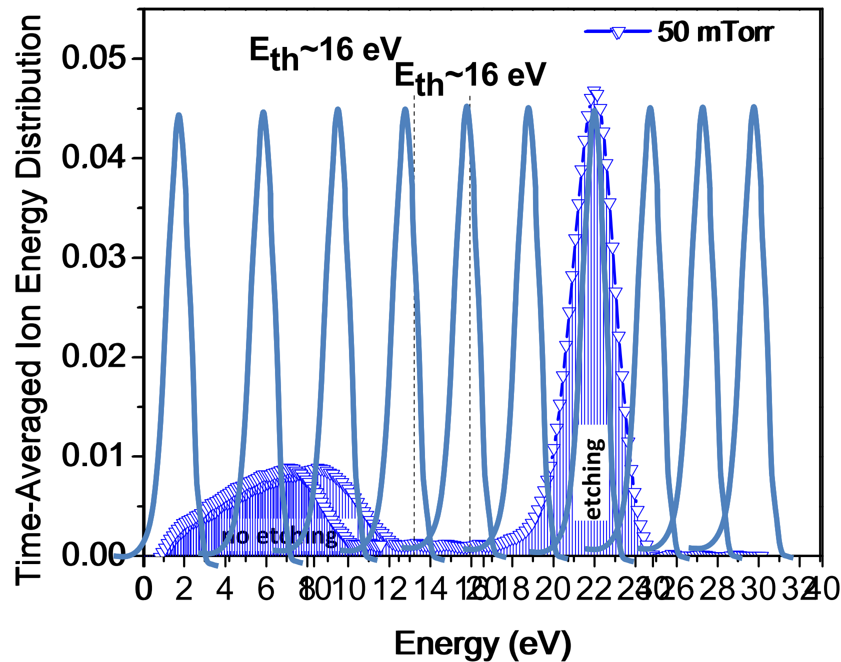
- Etching exhibits a threshold ion energy of 16 eV.

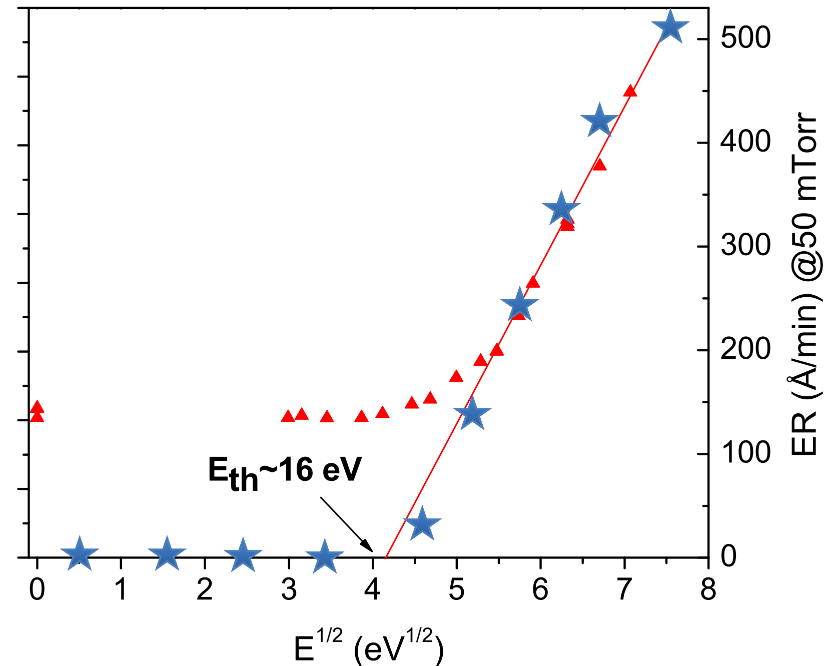
- Above this threshold, etching rate increases with the square root of ion energy.

"Kinetic study of low energy argon ion-enhanced plasma etching of polysilicon with atomic/molecular chlorine",
J. P. Chang, J. C. Arnold, G. C. H. Zau, H-S. Shin, and H. H. Sawin, J. Vac. Sci. Technol. A, **15**, 1853 (1997).



What We Expect in a Pulsed Plasma for Si Etching





- Ar/Cl_2 (few %) pulsed plasma.
- 20 μs ON 80 μs OFF.
- Synchronous DC bias in the afterglow at 70-97 μs.
- 10^{15} /cm^3 p-type Si

- Above threshold etching looks like what we expect.

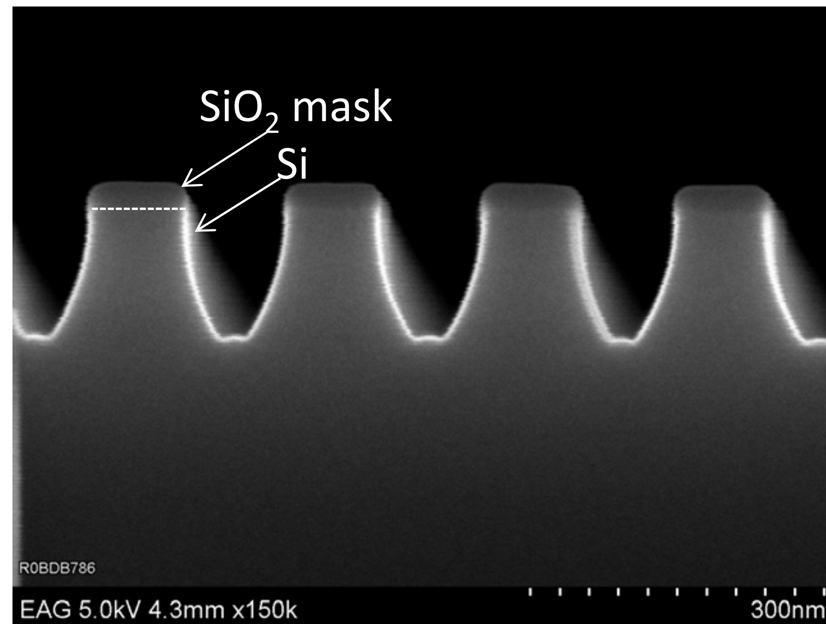
- **Big question (and big problem): What causes sub-threshold etching?**

What Causes Sub-threshold Etching?

- Spontaneous chemical etching by Cl atoms?

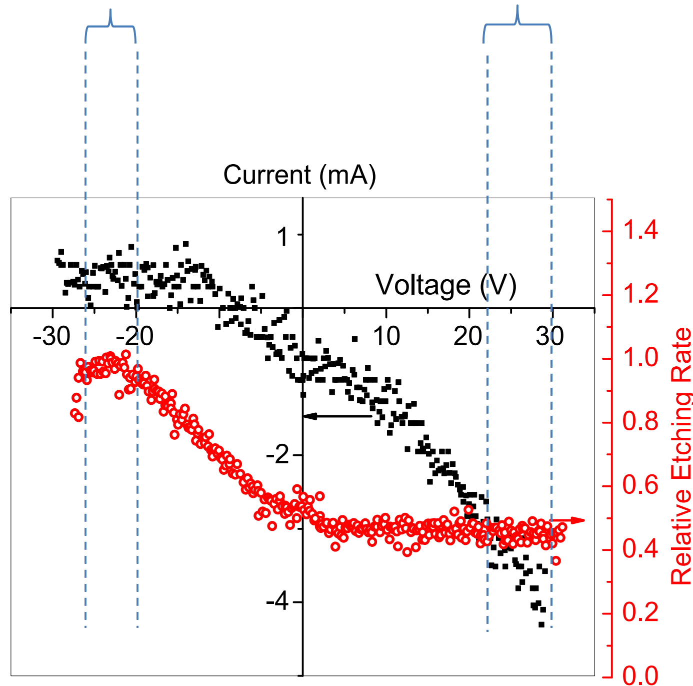
  - It is widely reported that this does not happen for p-type or i-Si (only heavily doped n-type).

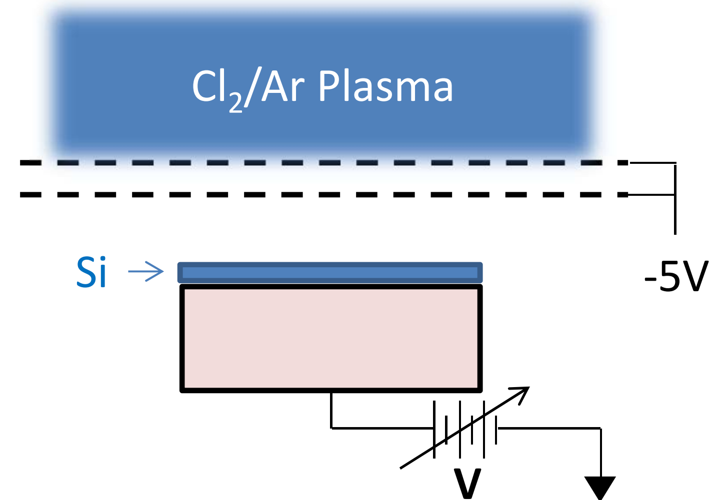
  - This is confirmed in our cross section SEMs: no undercutting of the mask.

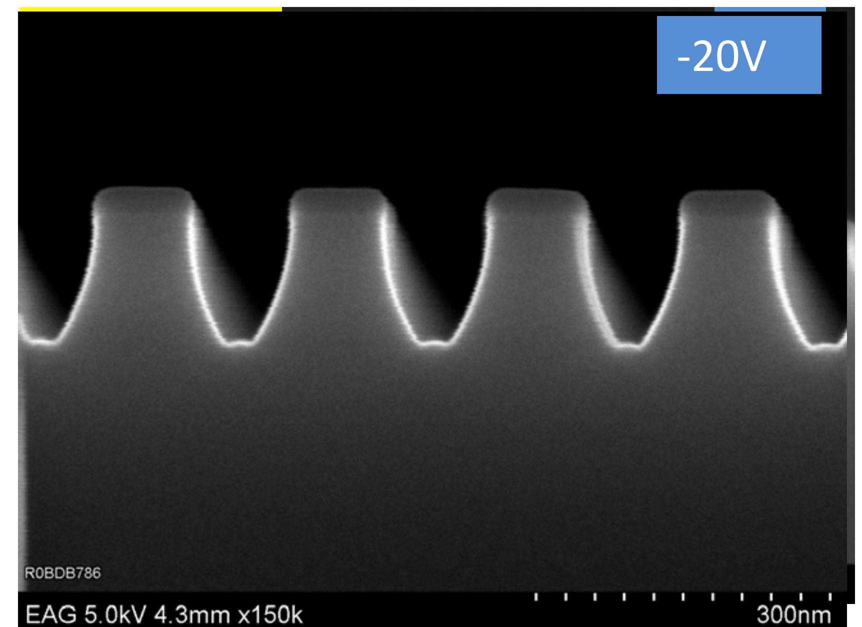


- Therefore spontaneous chemical etching by Cl atoms is <u>not</u> the reason.

Grids / Substrate Bias Experiments







<u>Conclusion</u>: Sub-threshold etching is due to photo-assisted etching induced by plasma light.

Summary

- After nearly 50 Years, plasma etching is well established yet challenges persist.
- As processes evolve to atomic layer etching, ion-induced lattice damage and mixing of etchant and substrate atoms present major problems, requiring controlled fluxes of low energy ions.
- Photo-assisted reactions also complicate etching with low energy ions.

More details can be found in:

- "Plasma Etching: Yesterday, Today, and Tomorrow", V. M. Donnelly and A. Kornblit, J. Vac. Sci. Technol. A, **31**, 050825-1 (2103).
- "Critical review: Plasma-surface reactions and the spinning wall method", V. M. Donnelly, J. Guha, and L. Stafford, J. Vac. Sci. Technol. A, **29**, 010801-1 (2011).
- "The surprising Importance of Photo-assisted Etching in Chlorine-Containing Plasmas", H. Shin, W. Zhu, C. M. Donnelly and D. J. Economou, J. Vac. Sci. Technol. A, **30**, 201306 (2012).
- "Review: Reactions of fluorine atoms with silicon, revisited, again", V. M. Donnelly, J. Vac. Sci. Technol. A, 35, 05C202-1 (2017).