Evaluation of ESH Impact for Plasma Etch: Etch By-Products

Matthew Radtke, Mark Nierode, J.W. Coburn, Dave Fraser and David B. Graves

Department of Chemical Engineering,
University of California, Berkeley

NSF/SRC ERC For Environmentally Benign Semiconductor Manufacturing

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Summary of Goals for Plasma Etch*

Characterize and minimize ESH impact of etch and chamber clean by-products and emissions, especially PFC's.

Develop plasma modeling and simulation methods to extend, generalize and integrate advances into a systems-level ESH/process development optimization.

Reduce plasma equipment energy use.

*** ITRS: ESH, FEP and Interconnect Chapters**

Challenge for Semiconductor Industry: Continued Scaling

- New device structures and new materials will be introduced into manufacturing over the next decade to achieve scaling goals
- Challenges in manufacturing will be in **simultaneously** optimizing for process objectives and ESH objectives
- Plasma etch appears to offer special challenges for several reasons:
  - plasma creates new materials: etch by-products
  - often observe by-product re-deposition on walls/wafer
  - plasma is unusually complex chemical environment complicating control strategies

New Materials: High and Low κ Dielectrics*

- ZrO_2, HfO_2, BST, TaO_5, Y_2O_3, (Zr, Hf, Ti,…)SiO_4, …
- SILK, organic polymers, polymer-SiO_2 composite, porous materials

***ITRS FEP and Interconnect Chapters**

Metal Gate Electrode Materials*

Required properties:

- Appropriate work function
- High T_m (>1000°C)
- Stable interface with gate dielectric
- Compatible with Si processing – deposition, etch

Candidate materials:

- High-T_m metals (Ta, Mo, Ru, W)
- metal nitrides (MoN, WN, TiN)
- doped metal oxides (In_2O_3, SnO_2, RuO_2)
- metal silicides (CrSi, WSi_x)

* T.J. King, ERC Retreat, 2001

Typical Etch Gases

- Cl_2, HCl, Br_2, HBr...
- O_2, N_2, H_2….
- CF_4, HCF_3, C_2F_6, C_4F_8, SF_6, NF_3,…. (PFC's & HFC's)
- CH_4, C_2H_6,….

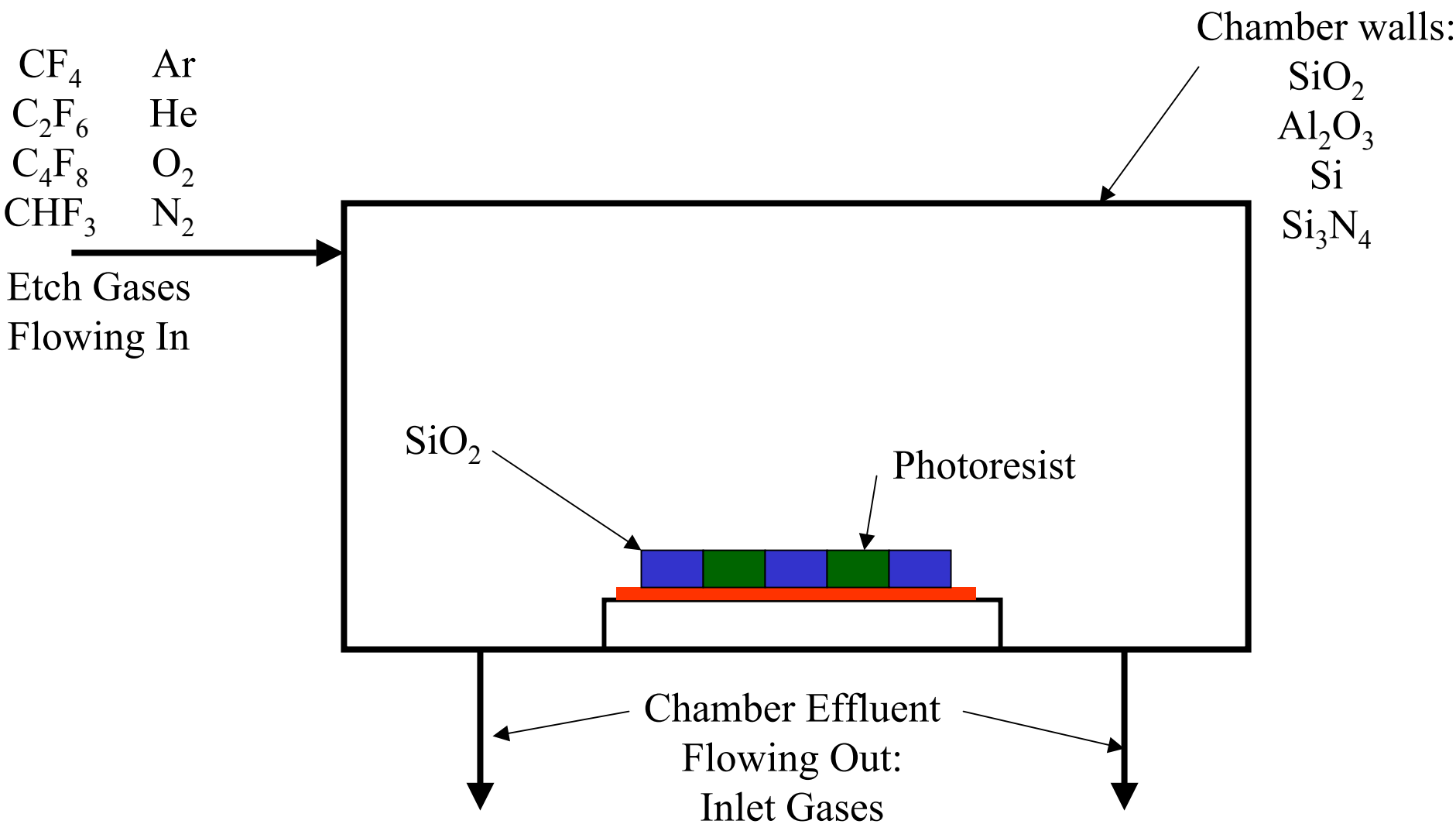
Many Possible New Materials/Etch Gases

- Clear need for a systematic approach
- Need methods to identify potential ESH-sensitive compounds formed during etch/clean
- Need methods to model or predict compound formation to minimize costs of examining all alternatives
- Need ways to combine process and ESH objectives optimization

Simultaneous Process and ESH Objective Optimization

- Etch by-products play central role in both process effects and ESH concerns
- Critical dimension and selectivity control in etch strongly affected by deposition or re-deposition of etch products and/or etch gas decomposition products
- Etch/chamber clean emissions control center around gas phase/wall species
- Project ***naturally combines process and ESH goals***

Etch Chamber with No Plasma



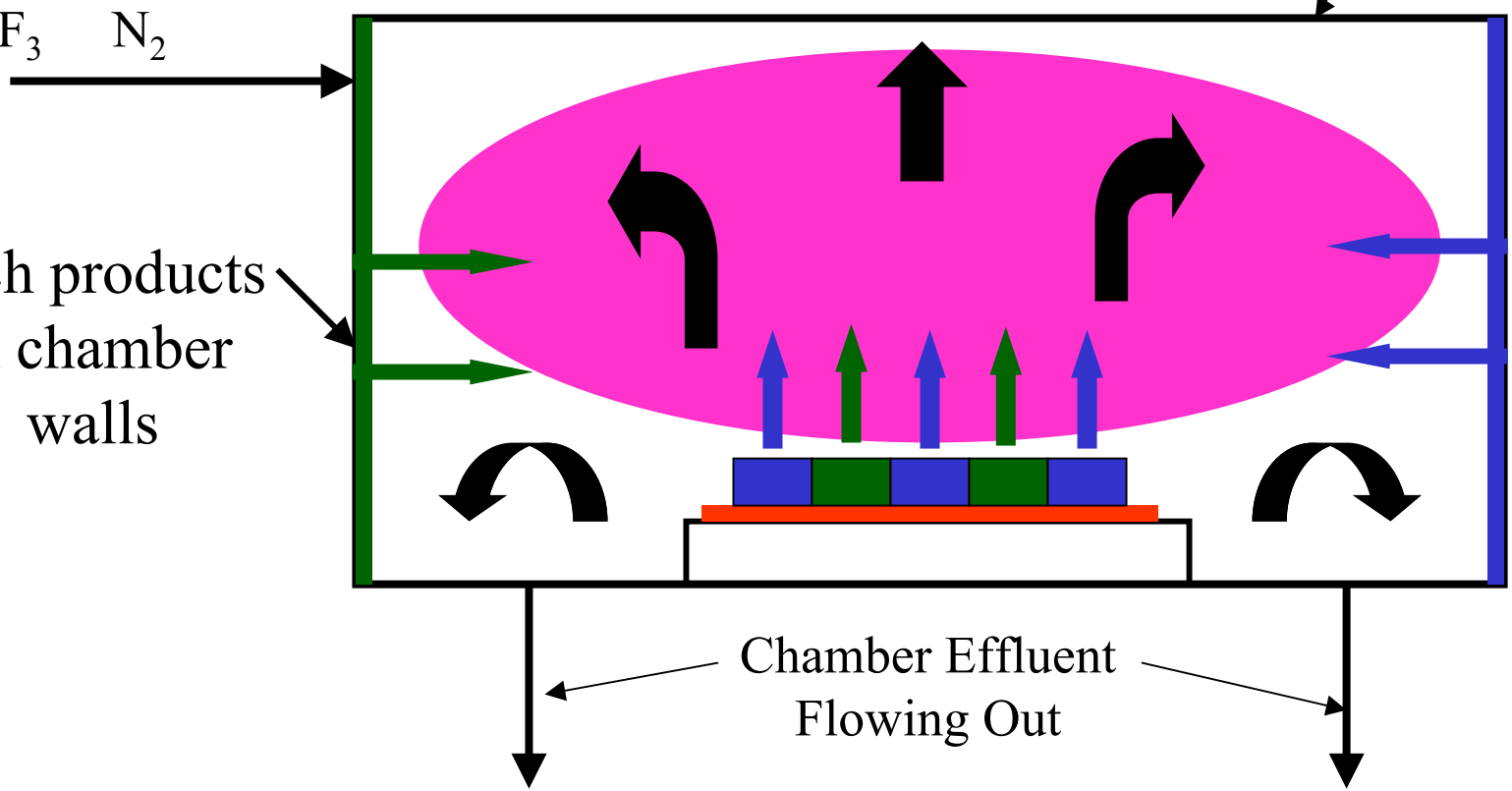
Etch Chamber with Plasma On

Plasma creates all possible combinations of inlet gas, film, and chamber wall materials

Etch Gases Flowing In

CF_4	Ar
C_2F_6	He
C_4F_8	O_2
CHF_3	N_2

Chamber walls:
SiO_2
Al_2O_3
Si
Si_3N_4

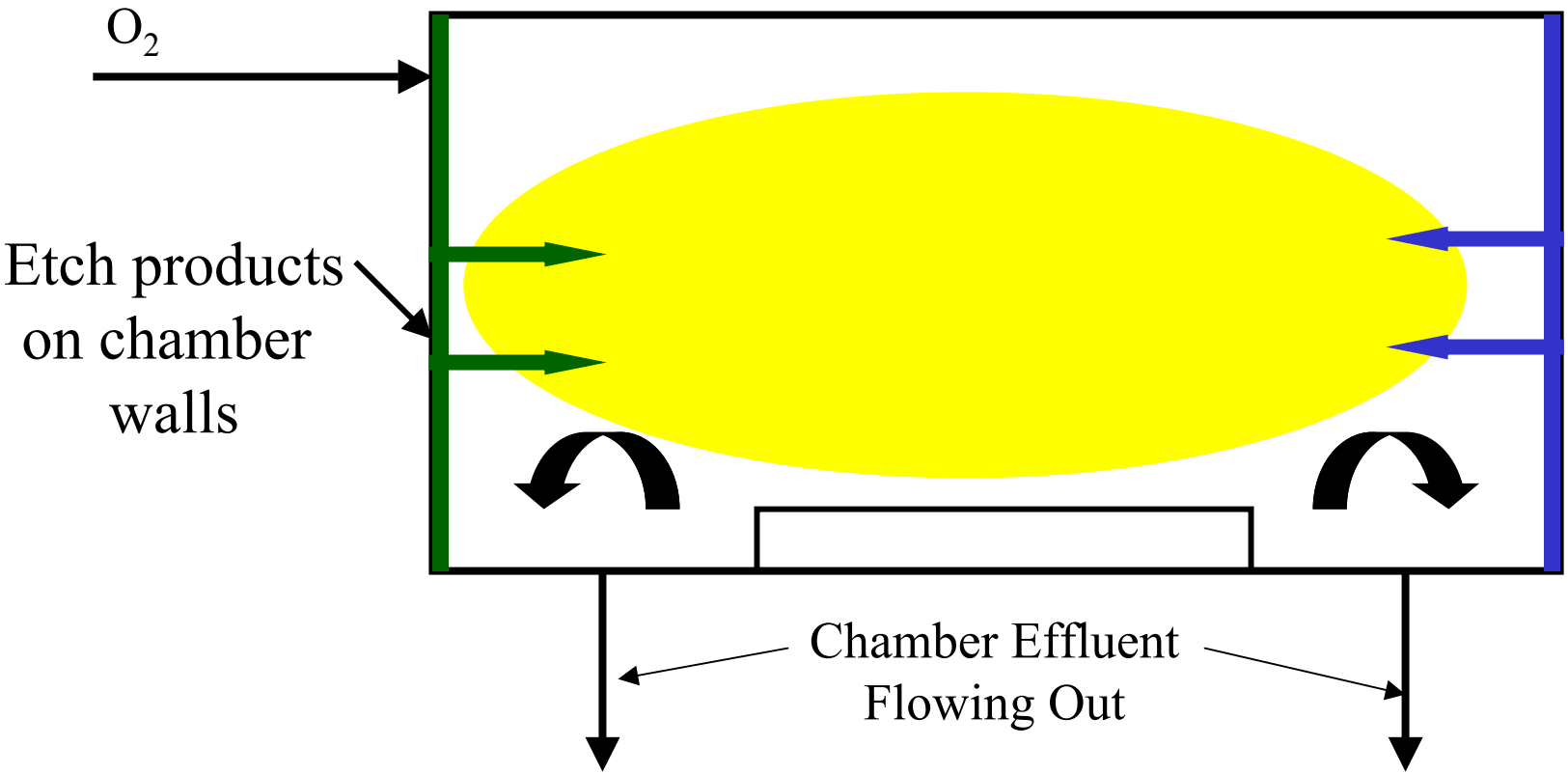


Etch Chamber with Plasma On: Chamber Wall Cleaning

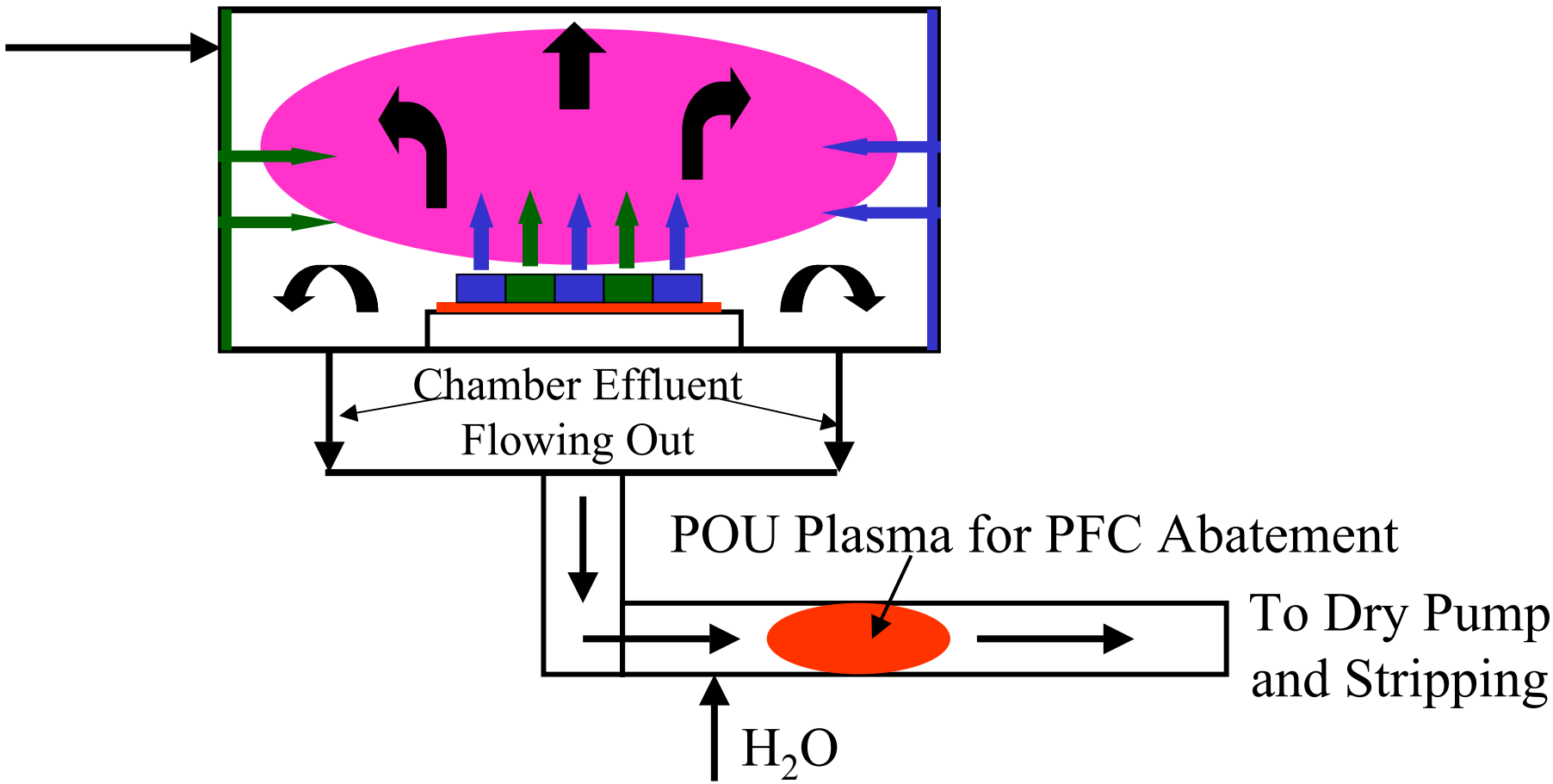
Clean Gases Flowing In

Ar
SF_6
O_2

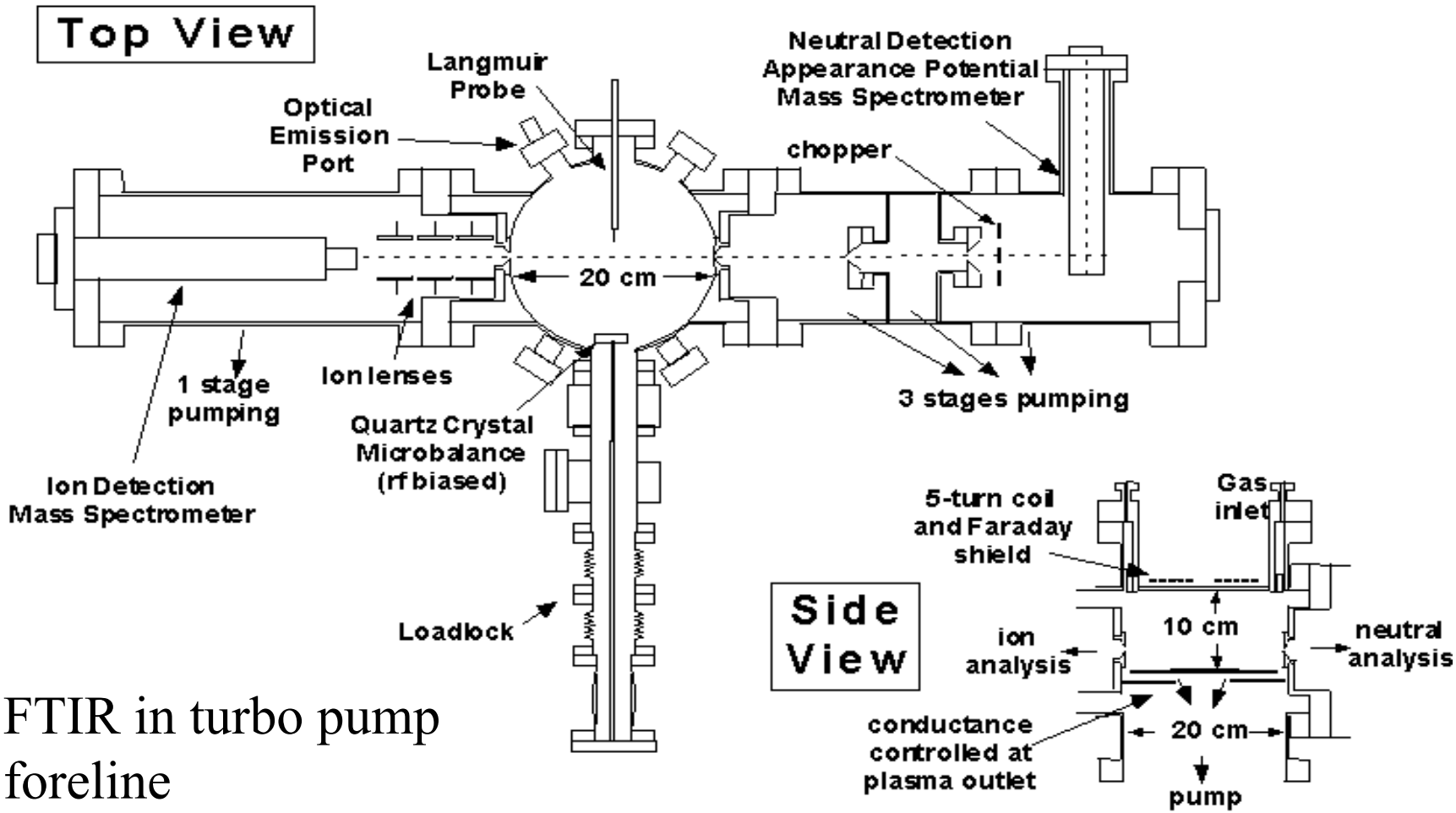
New set of chemistries during chamber clean



Downstream Plasma: POU Plasma Abatement in Foreline

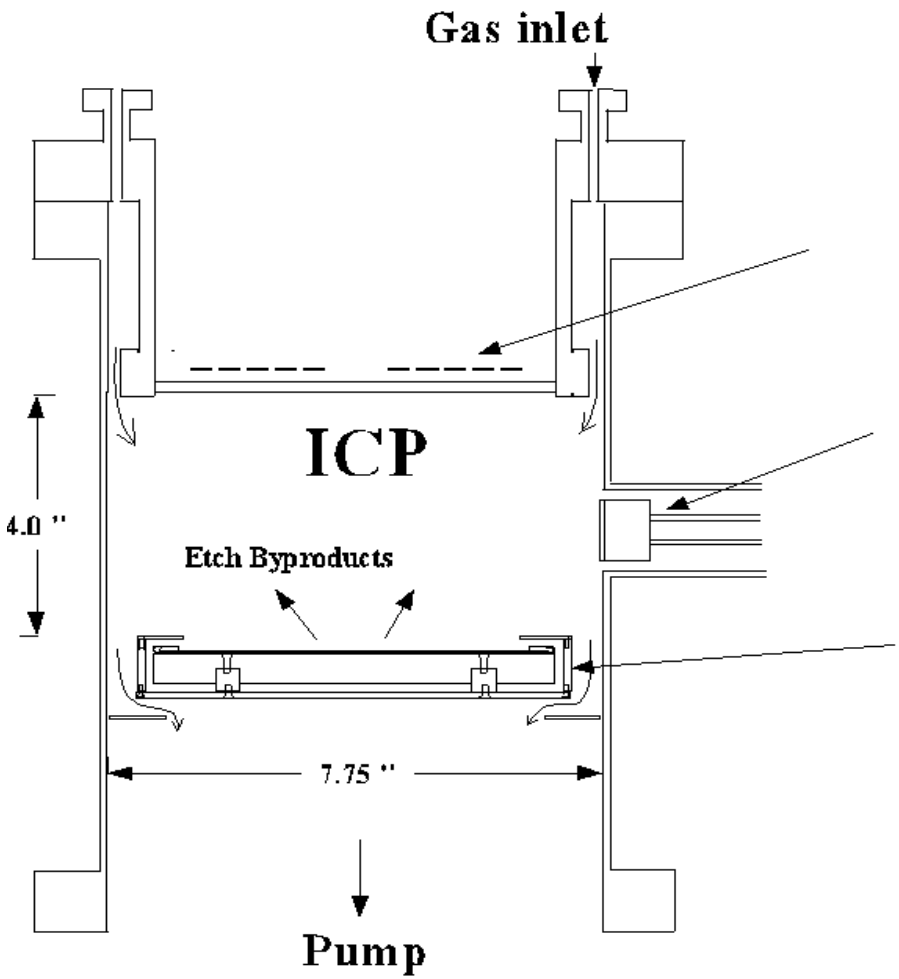


Experimental Apparatus



FTIR in turbo pump foreline

Etch Chamber (side view)



5-turn coil and
Faraday shield

Quartz Crystal Microbalance
- etch rate measurement
- rf biased
- loadlock

Chuck
- release etch byproducts into plasma
- shielded
- rf biased

Preliminary Experimental Results: $Si/Cl_2/O_2$

- Si etch to establish base case for comparison to proposed metal gate electrode materials
- What happens to etch products?
  - What fraction of etch products ionize?
  - What fraction of positive ions contain etch products?
- Important question to address is extent of etch product re-deposition on chamber walls (and therefore on wafer)

Strategy

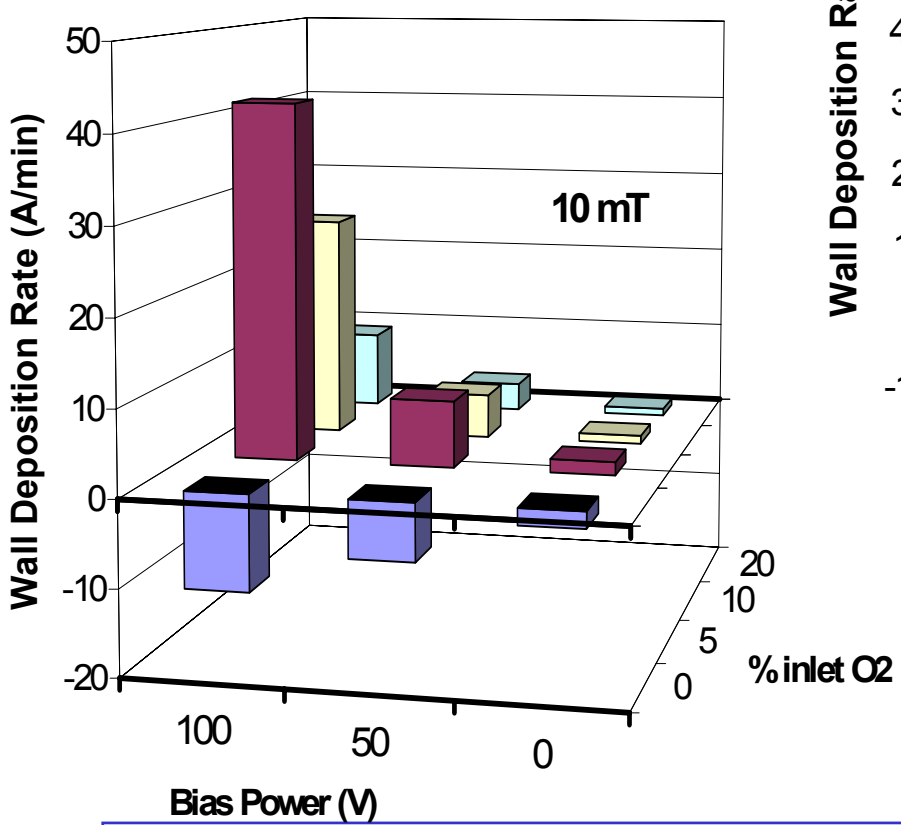
- Study system in which we know etch product re-deposition occurs: Si etching w/ O_2/Cl_2
- Measure wall deposition rates and corresponding ion and neutral fluxes to establish re-deposition mechanism.

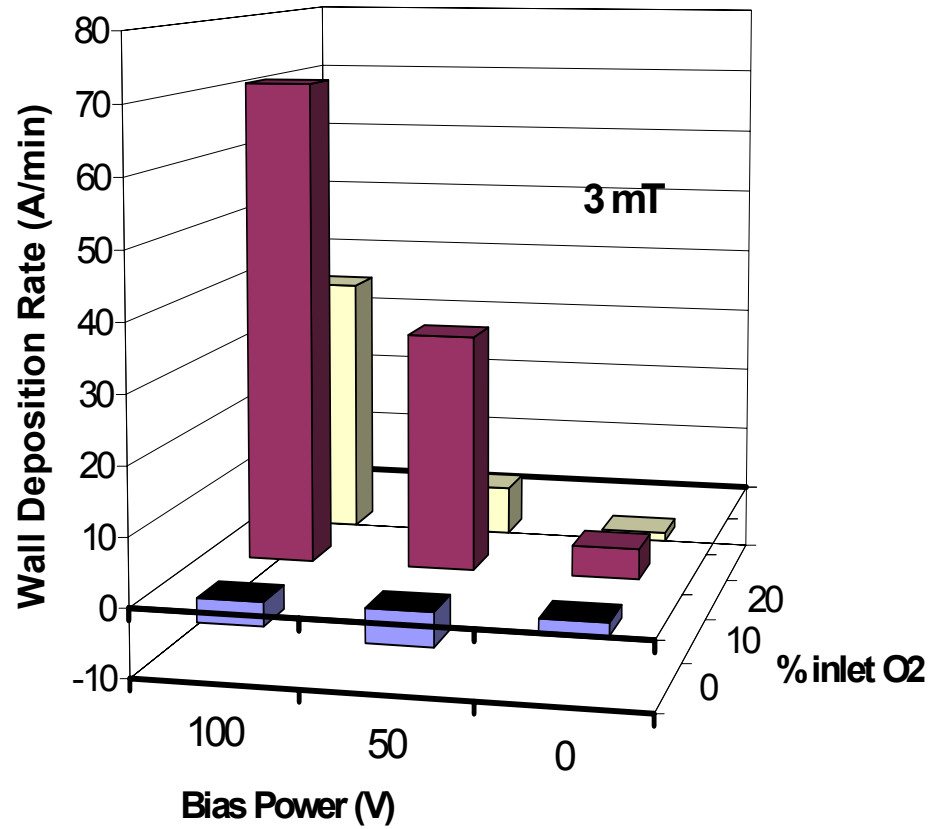
Experimental Conditions

Pressure: 3, 10 mT
Substrate Bias: 0, -50, -100V
Coil Power (deposited): 150 W
Inlet Gas Composition: Cl_2 & O_2 : 0, 5,10, 20% O_2
(3mT ~ 8 sccm, 10mT ~ 20 sccm)
*1-2 sccm of He backside wafer cooling

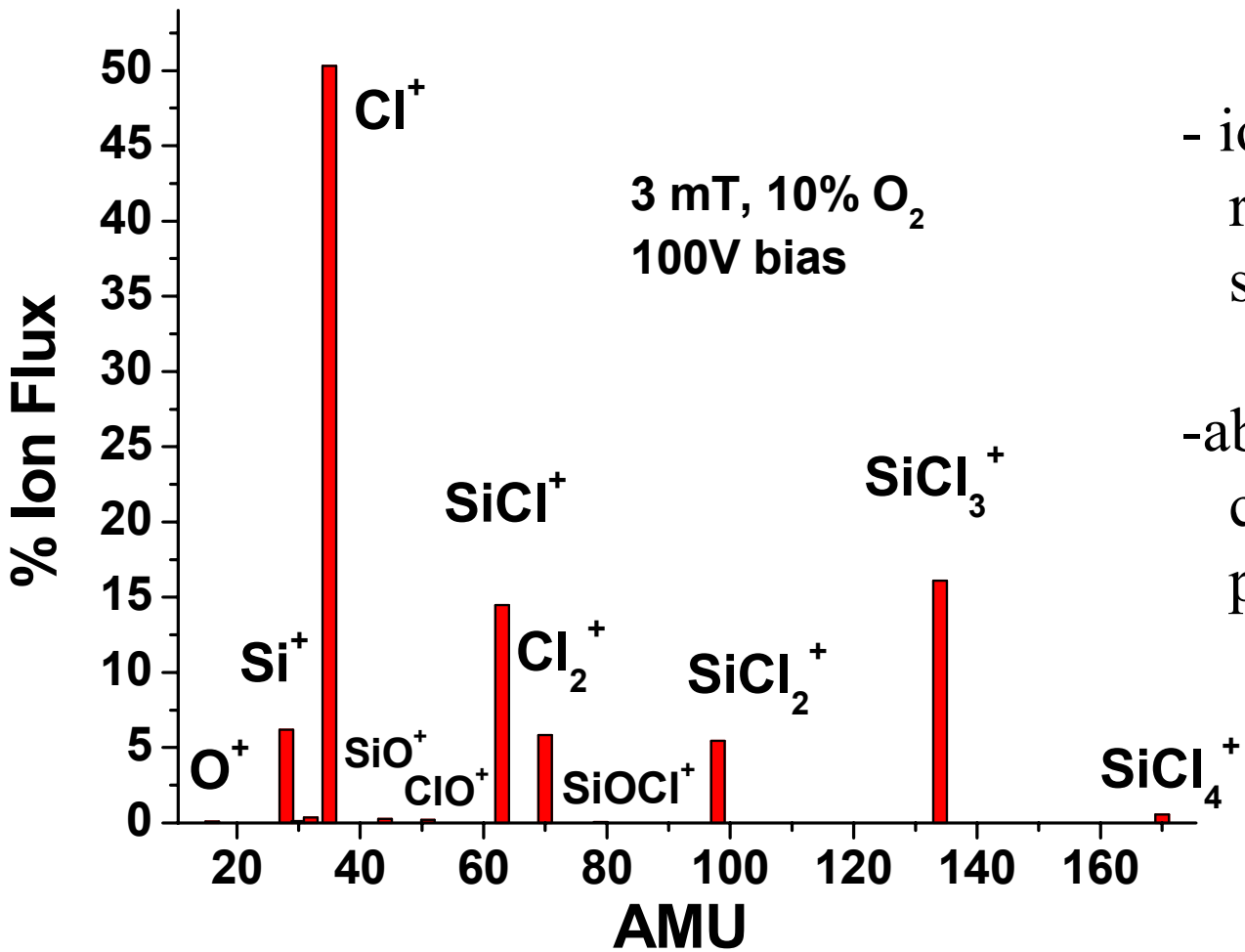
SiOCl Wall Deposition Rates

- maximum deposition rate with bias (wafer etching) and O_2 added





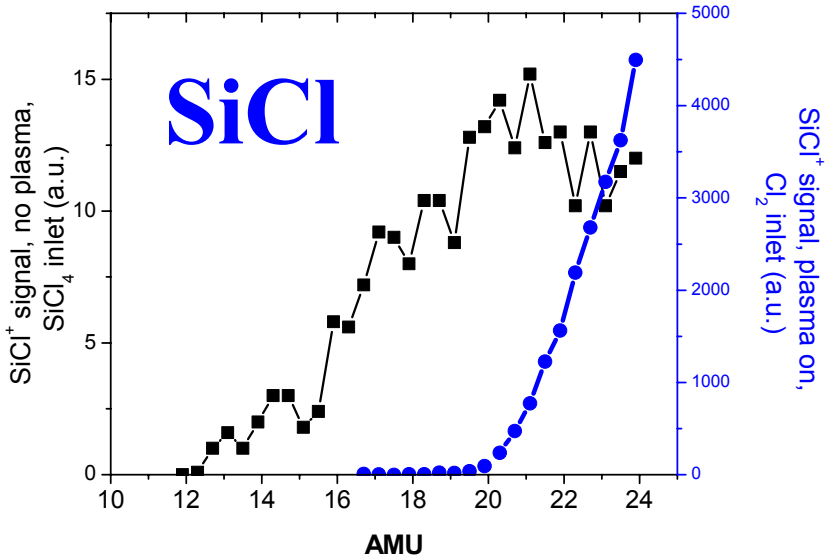
Ion Flux to Walls

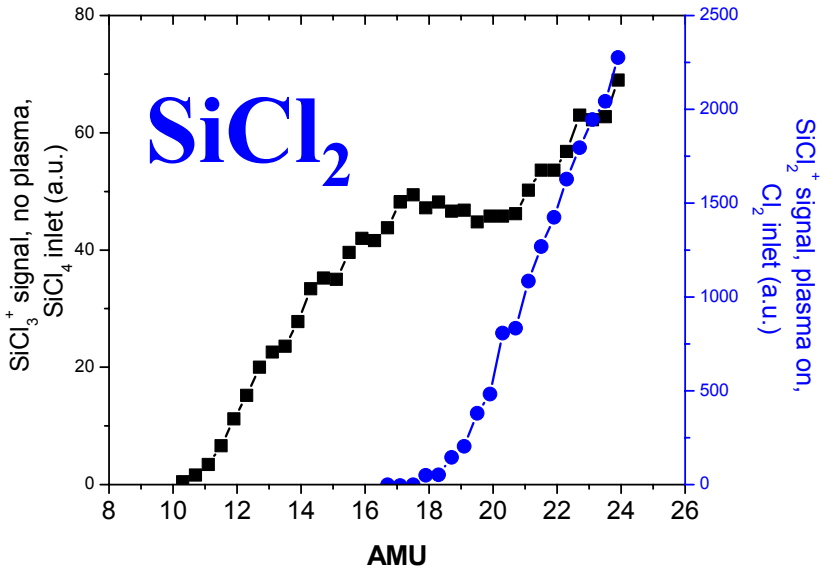


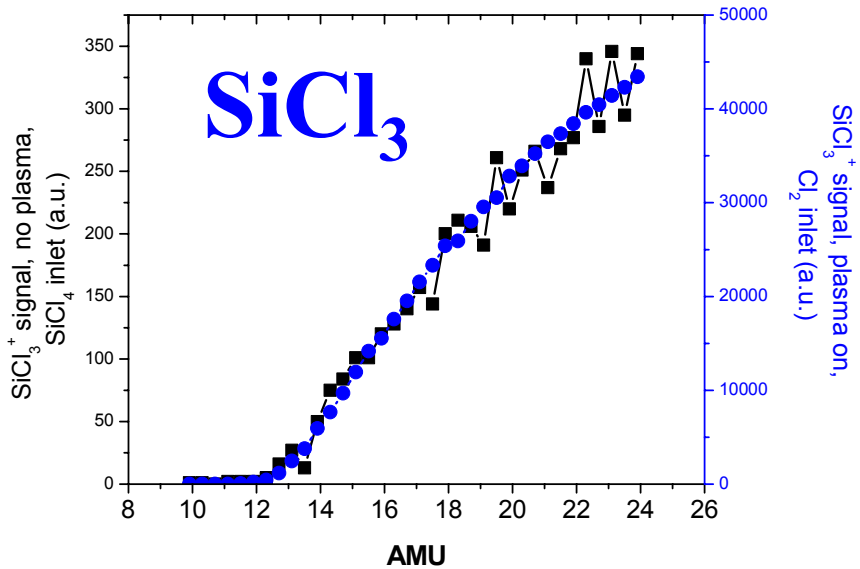
- ion composition ranged from 0-63% silicon-containing

-absolute ion fluxes calibrated from ion probe

APMS on $SiCl_x$ Neutral Species

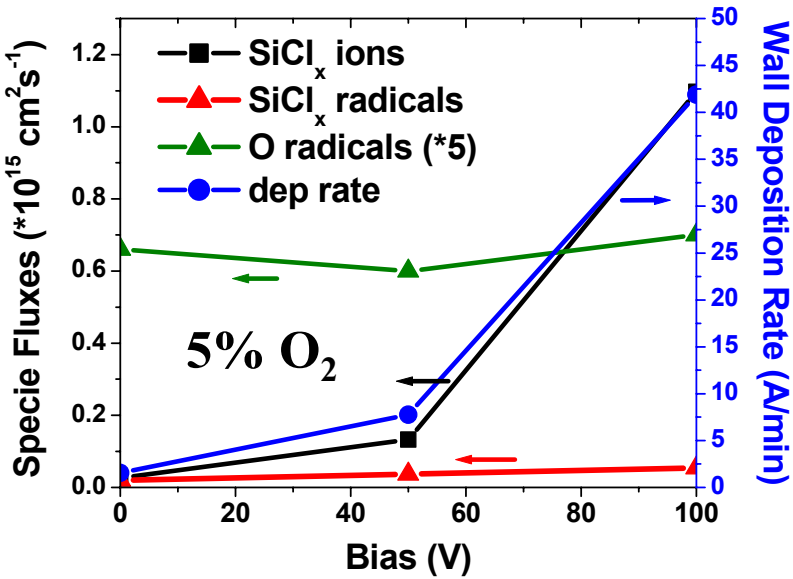


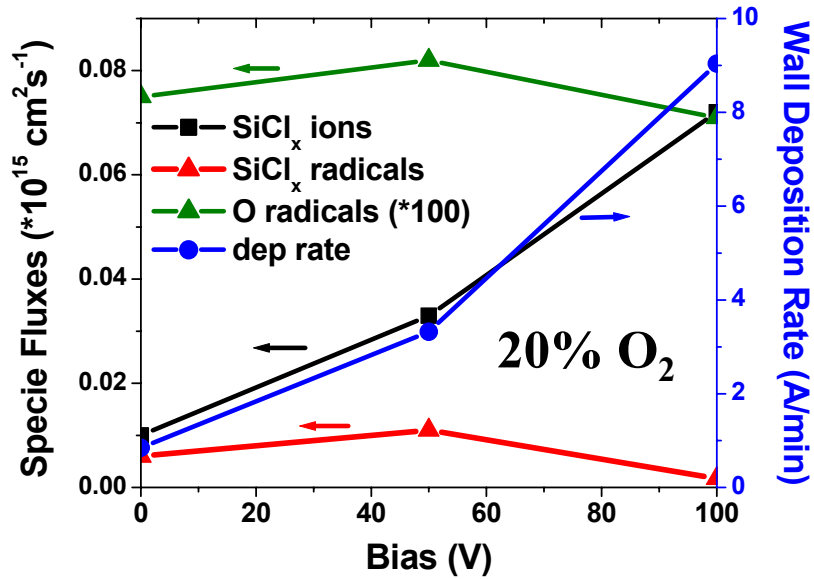


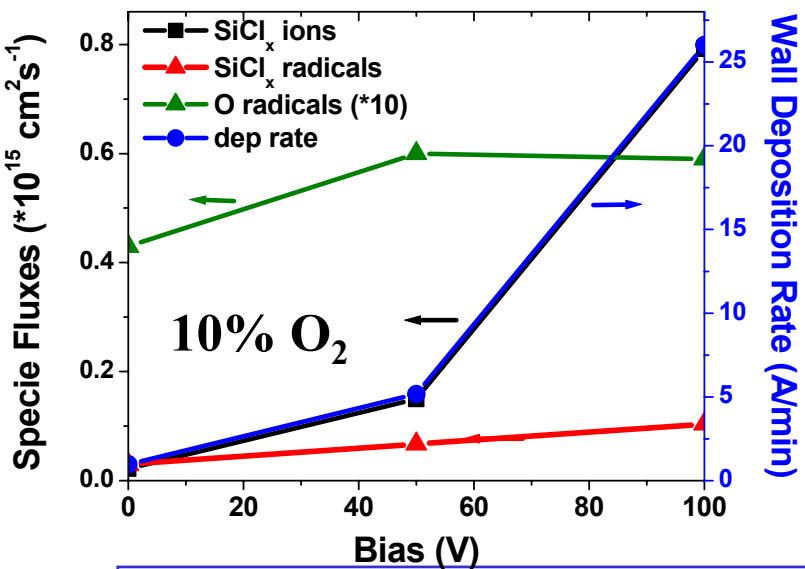


- SiCl and $SiCl_2$ are dominant $SiCl_x$ radicals
- no $SiCl_3$ observed at experimental conditions (trace SiClO observed)

Deposition Rate vs. Incident Flux (10 mTorr)





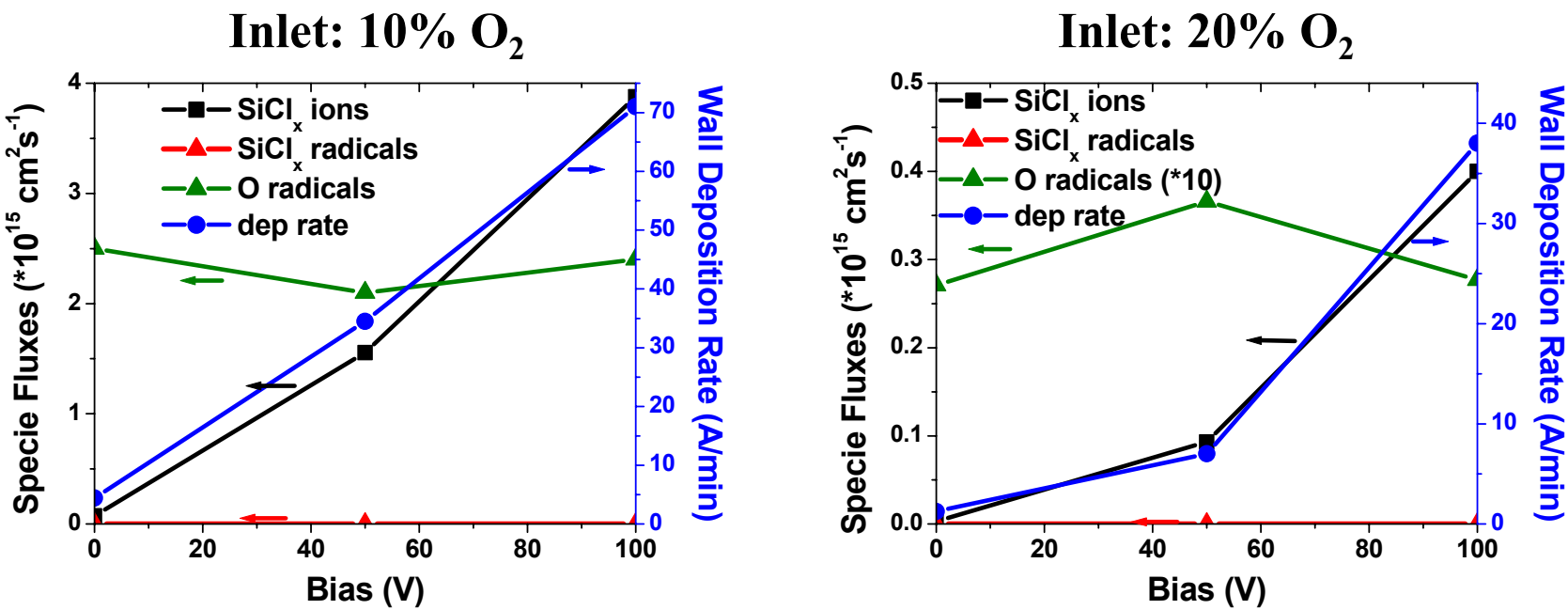


- $R_{growth} \propto \Gamma_{SiCl_x^+}$

  $\Gamma_o >> \Gamma_{SiCl_x}$

- Absolute radical fluxes estimated from radical direct ionization cross sections

Deposition Rate vs. Incident Flux (3 mTorr)



- $R_{growth} \propto \Gamma_{SiCl_x^+}$; $\Gamma_o >> \Gamma_{SiCl_x^+}$; ion mass flux can account for wall mass increase

Major conclusion: SiOCl wall deposition strongly correlates with surface flux of Si-containing positive ions

Similar Studies for Other Materials: e.g. Metal Gate Electrode Etch

- New metal gate materials may create various unknown toxic/hazardous by-products during etching

- Similarly to Si, these materials are likely to ionize readily in plasma (metals generally have low ionization potentials)

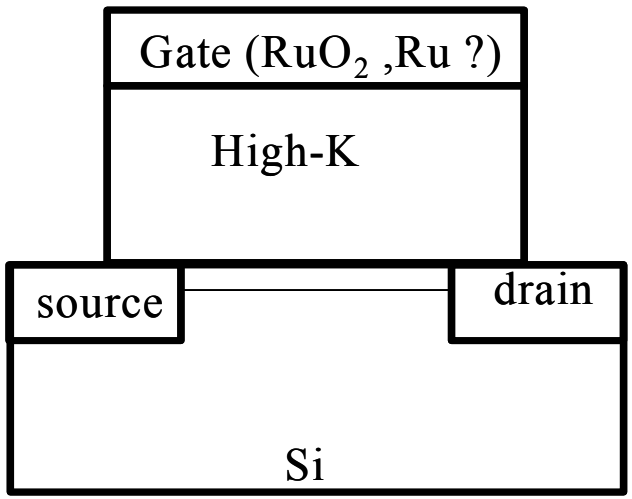
- Look for correlation between etch-product-containing ions and wall re-deposition

- Examine wall deposit composition

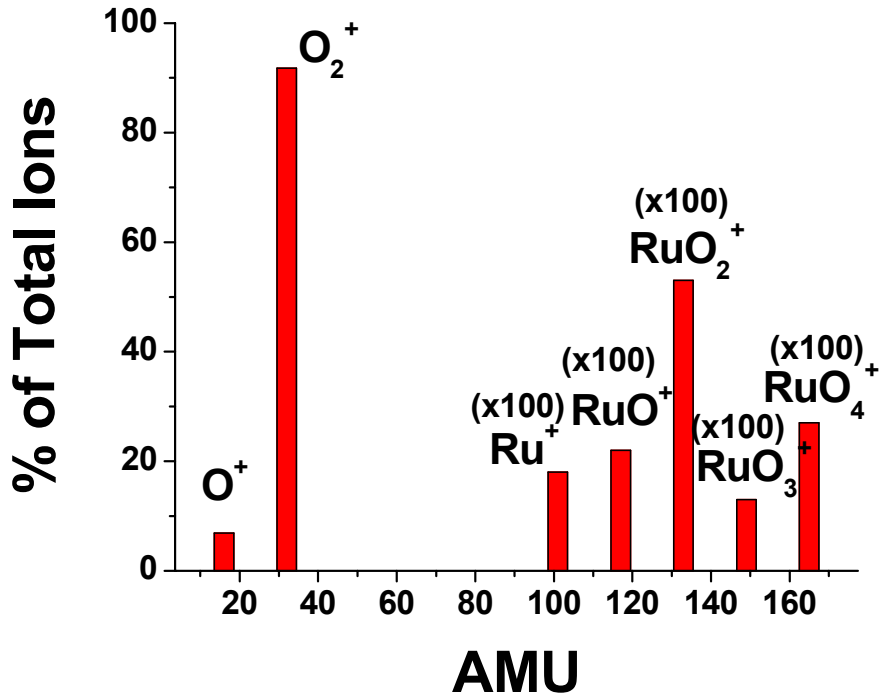
- Look for neutral volatile species that might pose ESH risk

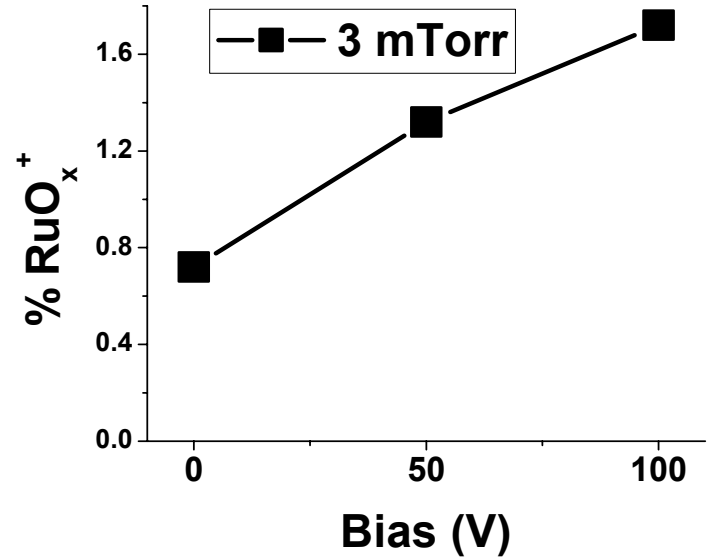
RuO_2 Etching in O_2-Containing Plasma

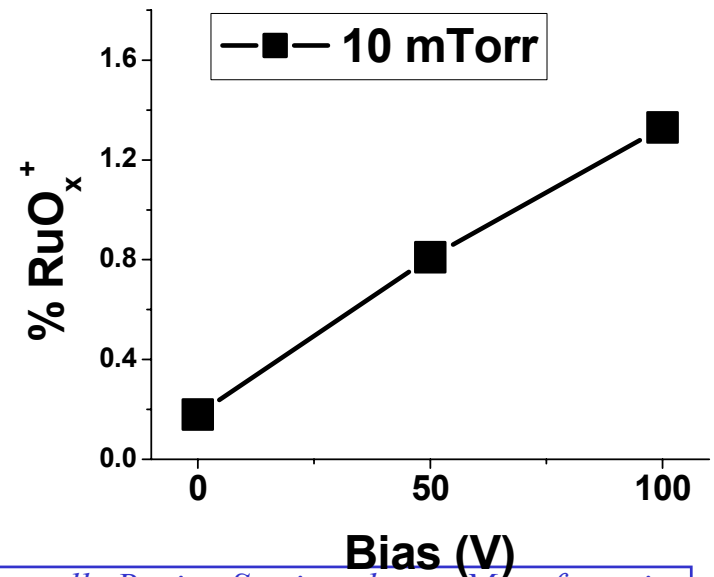
- Ru, RuO_2 are potential metal gate electrode materials for use with high k gate dielectrics
- Do etch by-products contain RuO_4 ? Is it formed in plasma?
- RuO_4 major concern for toxicity: minimize formation/emission



Plasma Composition: Ions



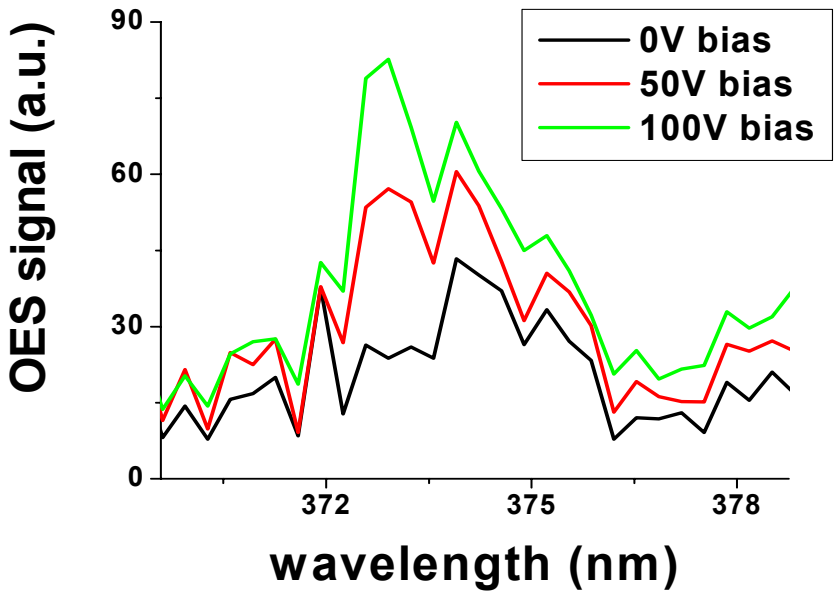




- 0-2% of ions contained Ru
- significant Ru etched w/out bias

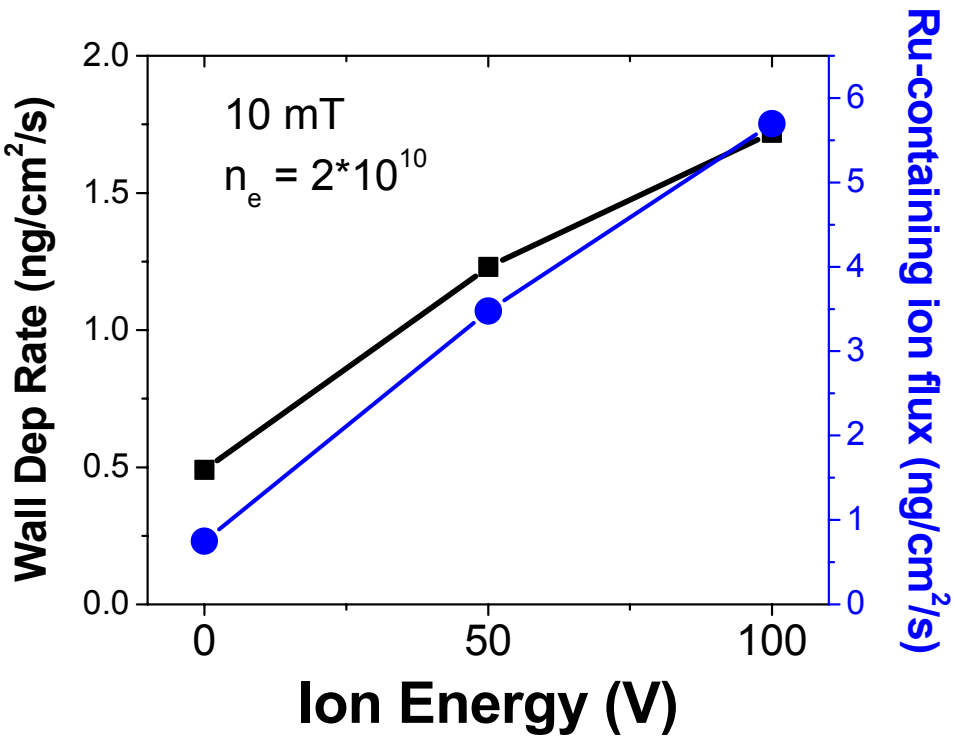
* temperature dependent

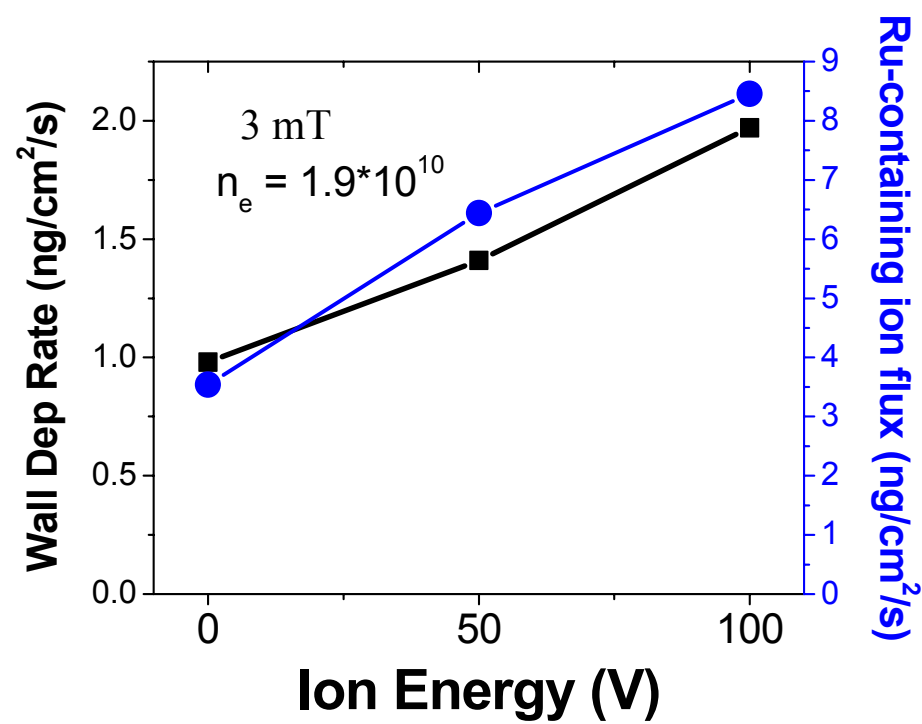
Plasma Composition: Neutrals



- trace amounts of Ru (372.8nm) observed with OES
- APMS detected trace amount of Ru; no RuO_x neutrals detected
- neutral Ru species may be nearly completely ionized: low ionization potentials (Ru: 7.37eV)

Ru Ion Flux and Wall Deposition Rate





- Deposition rate proportional to RuO_x^+ ion mass flux to surface
- Ion mass flux to wall ~ 3-4X greater than deposition rate, implying some deposited Ru is re-etched or ion sticking probability not unity

Concluding Remarks

1. Etch product ionization followed by wall deposition appears to be a dominant mechanism for etch product transport in many etch chemistries. (Evidence in ZrO_2 etch for Zr-wall deposition presented by Jim McVittie and co-workers at Stanford).
2. This limits flow of potentially toxic/hazardous materials to foreline and fab exhaust systems, e.g. RuO_4 appears not to leave chamber in detectable quantities during RuO_2 etch.
3. However, wall deposits pose potential risks to operators.
4. Chamber wall cleaning must also be studied: wall-deposited etch product removal important for tool effectiveness, energy and consumables, as well as potential ESH impact.

Concluding Remarks, Continued

5. Wall deposit composition needs to be measured.
6. Many more materials must be studied.
7. Major challenge: obtain new materials in significant quantities for etch studies.
8. Development of etch by-product models under development, continuing the work of former ERC student Mark Kiehlbaugh (Lam Research).

Acknowledgements

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