Vacuum Beam Studies of Radical-Surface and Ion-Surface Interactions

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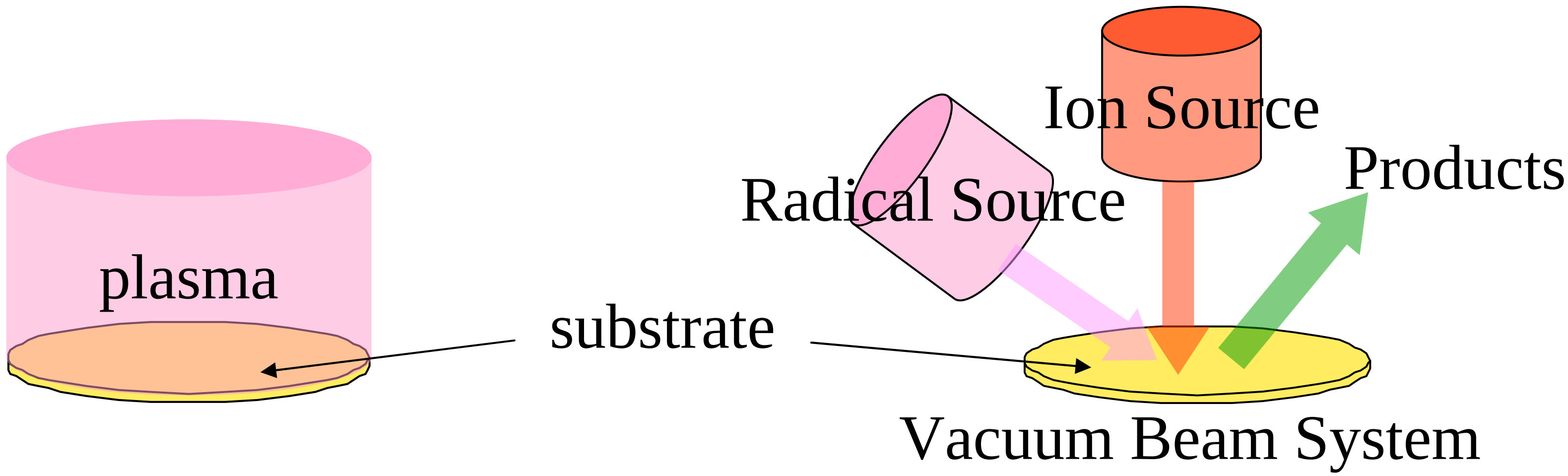
Vacuum Beam Systems



- Gas phase and surface chemistries are coupled

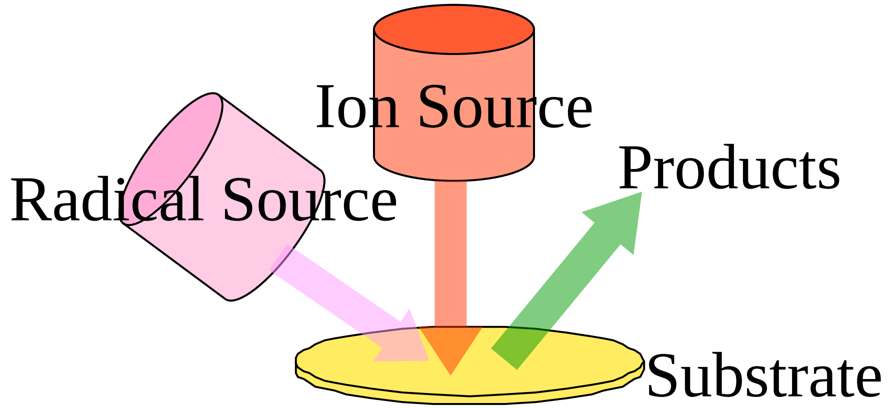
- Difficult to determine the reactants and products

- De-couple the gas phase and surface chemistry

- Determine the individual and synergistic effect of neutral and ion species on the substrate

- Determine the products

Vacuum Beam Studies

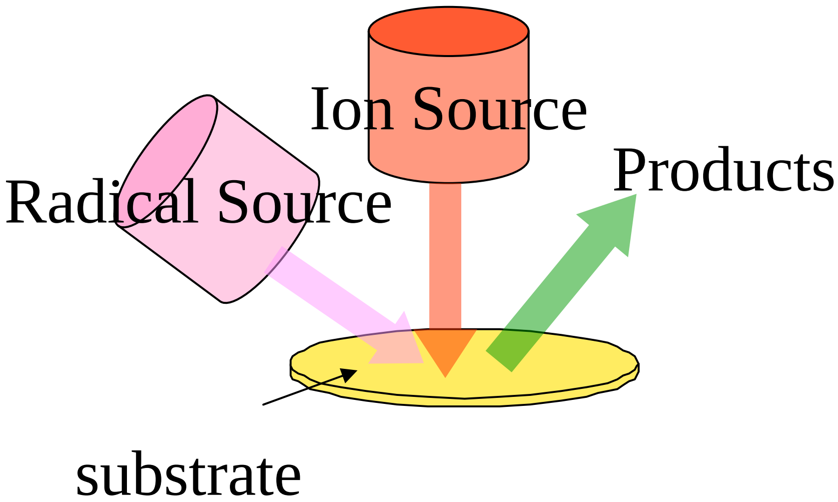


- Substrate is placed in a high vacuum chamber
  - No gas phase collisions between the radicals and ions from the sources and the products
  - Neglect gas phase chemistry

3 key measurements:

- Characterization of the species flux from the sources to the surface
- *In situ* substrate modification detection
- Characterization of the product from the surface reaction or the reflected species

Current Vacuum Beam System



- Commercial radical source
  (Oxford Applied Research)
- Commercial ion source
  (RBD Electronics)

For the 3 key measurements:

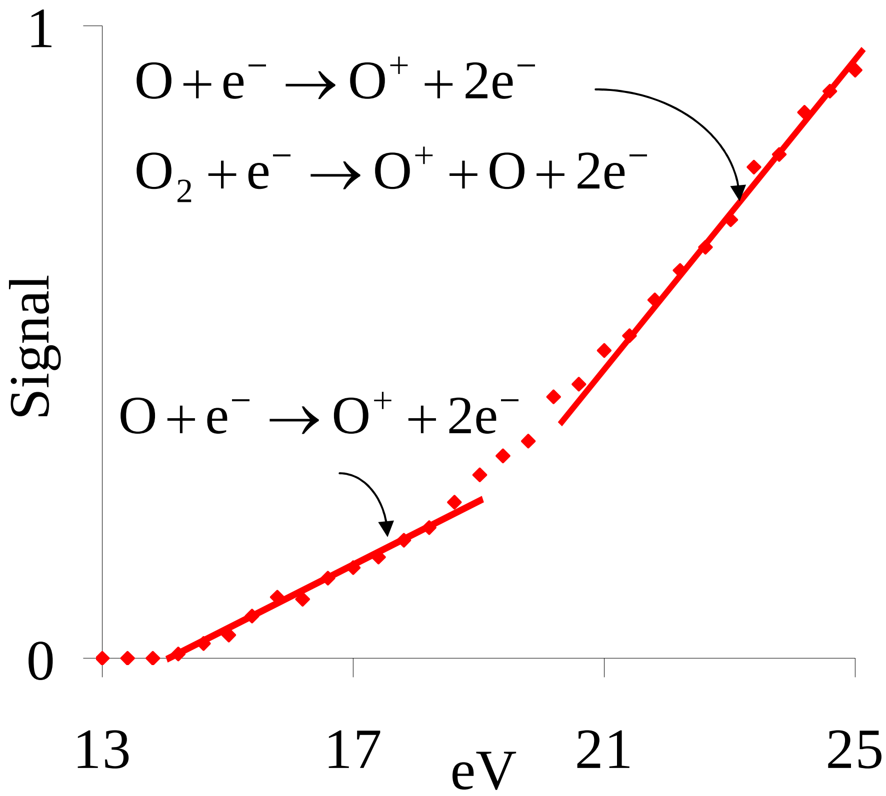
- Threshold ionization mass spectrometer (TIMS) for radical fluxes
- Faraday cup for ion flux
- Quartz crystal microbalance (QCM): *in situ* etch/deposition rate
- Attenuated total internal reflectance Fourier transform infrared spectroscopy (ATIR-FTIR): *in situ* surface function groups
- TIMS to detect reflected and desorbed species from the surface

Threshold Ionization Mass Spectrometry

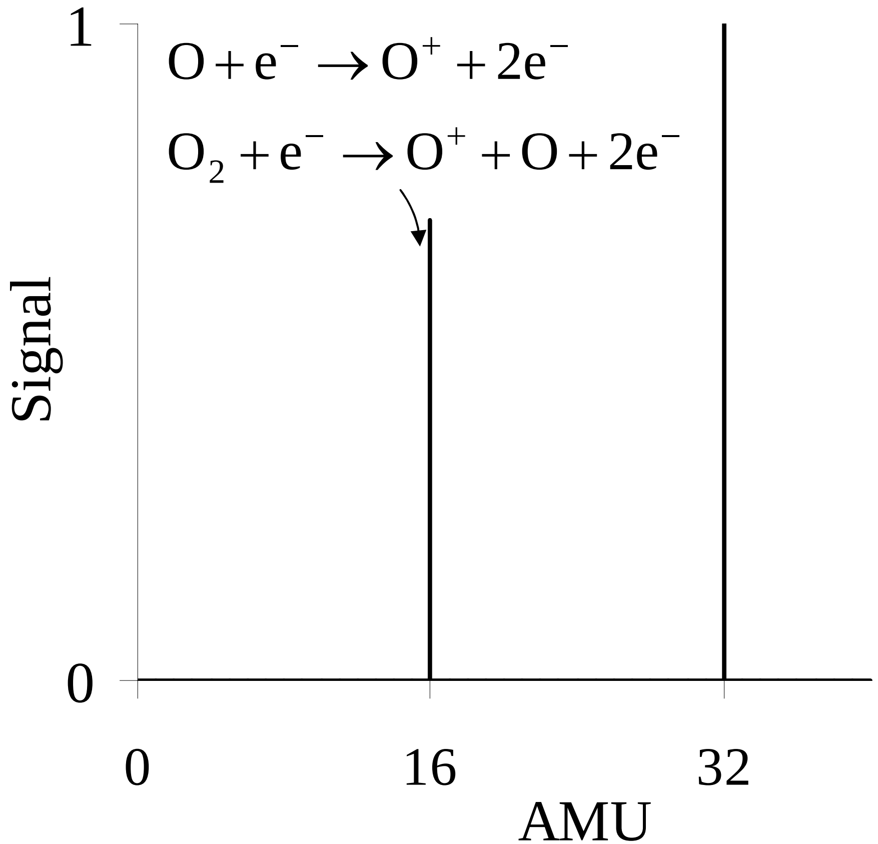
$O + e^- \rightarrow O^+ + 2e^-$ $E_{O \rightarrow O^+}$=14 eV Direct Ionization[1]

$O_2 + e^- \rightarrow O^+ + O + 2e^-$ $E_{O_2 \rightarrow O^+}$=20 eV Dissociative Ionization[2]

TIMS: 16 AMU signal

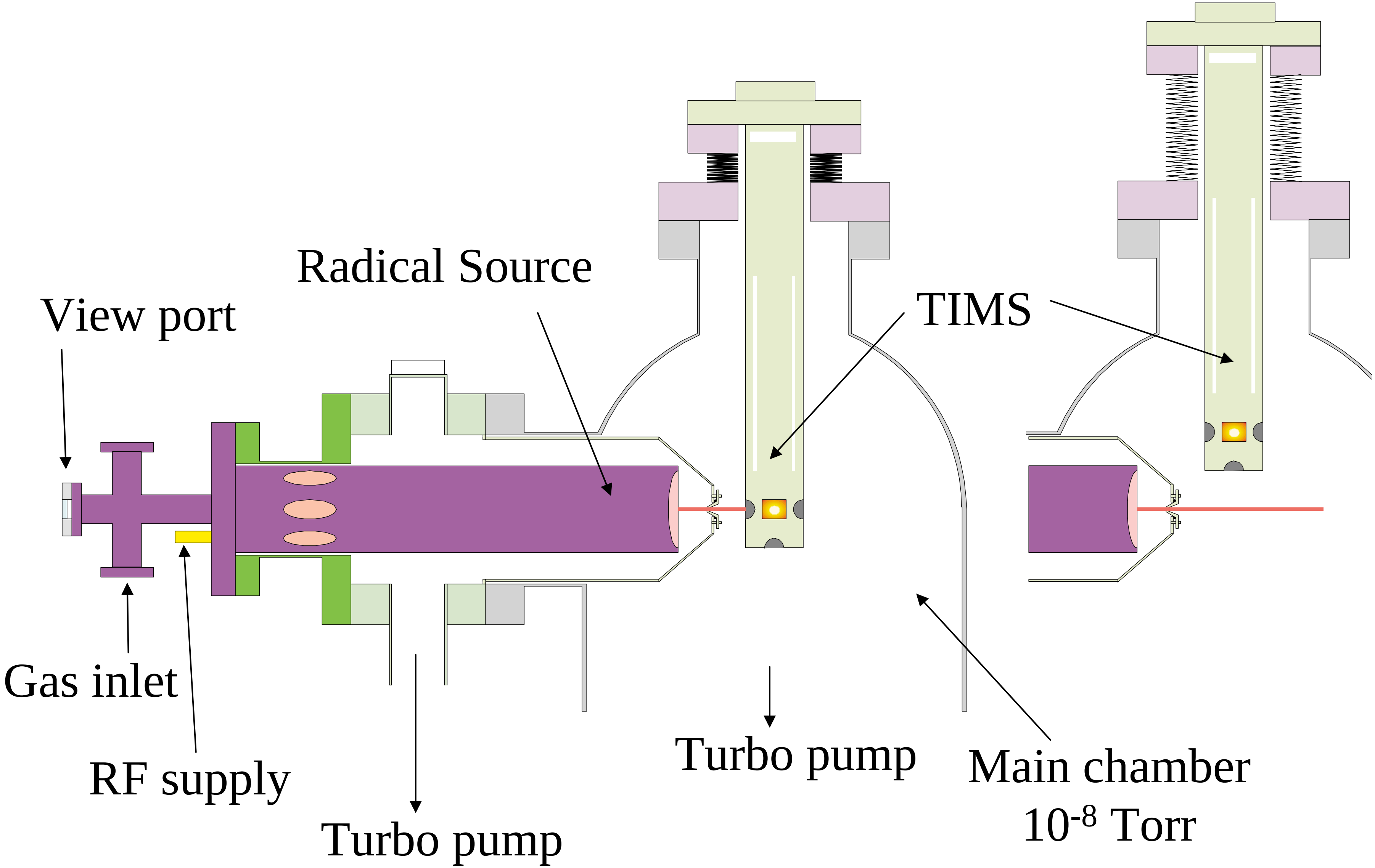


MS: 70 eV

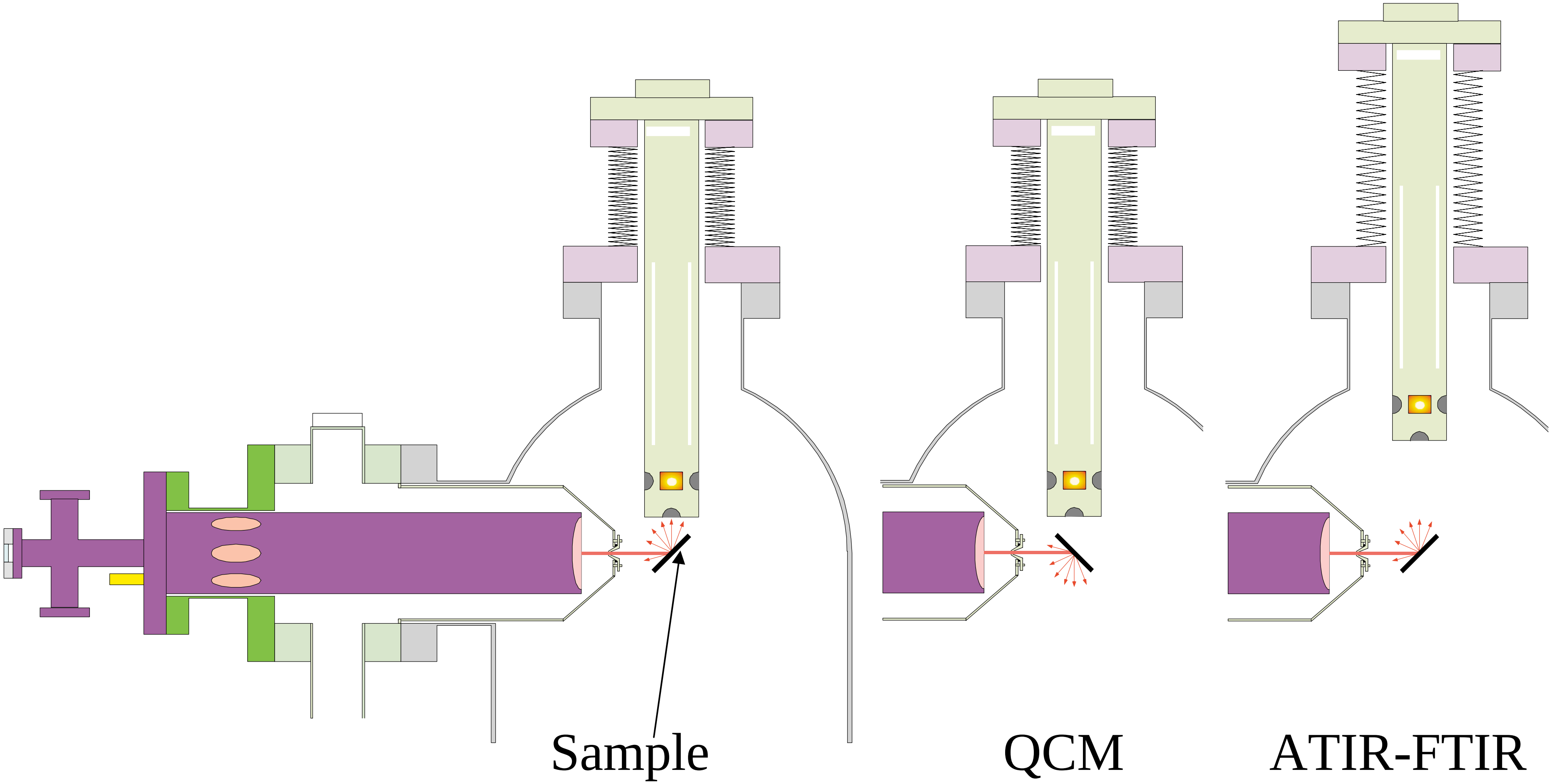


1 Brook, E., *et. al.*, *J. Phys. B*, Vol. 11, 1978. 2 Krishnakumar E., *et. al.*, *Int. J. Mass. Spc. Ion. Proc.*, Vol. 113, 1992.

Radical Flux Determination



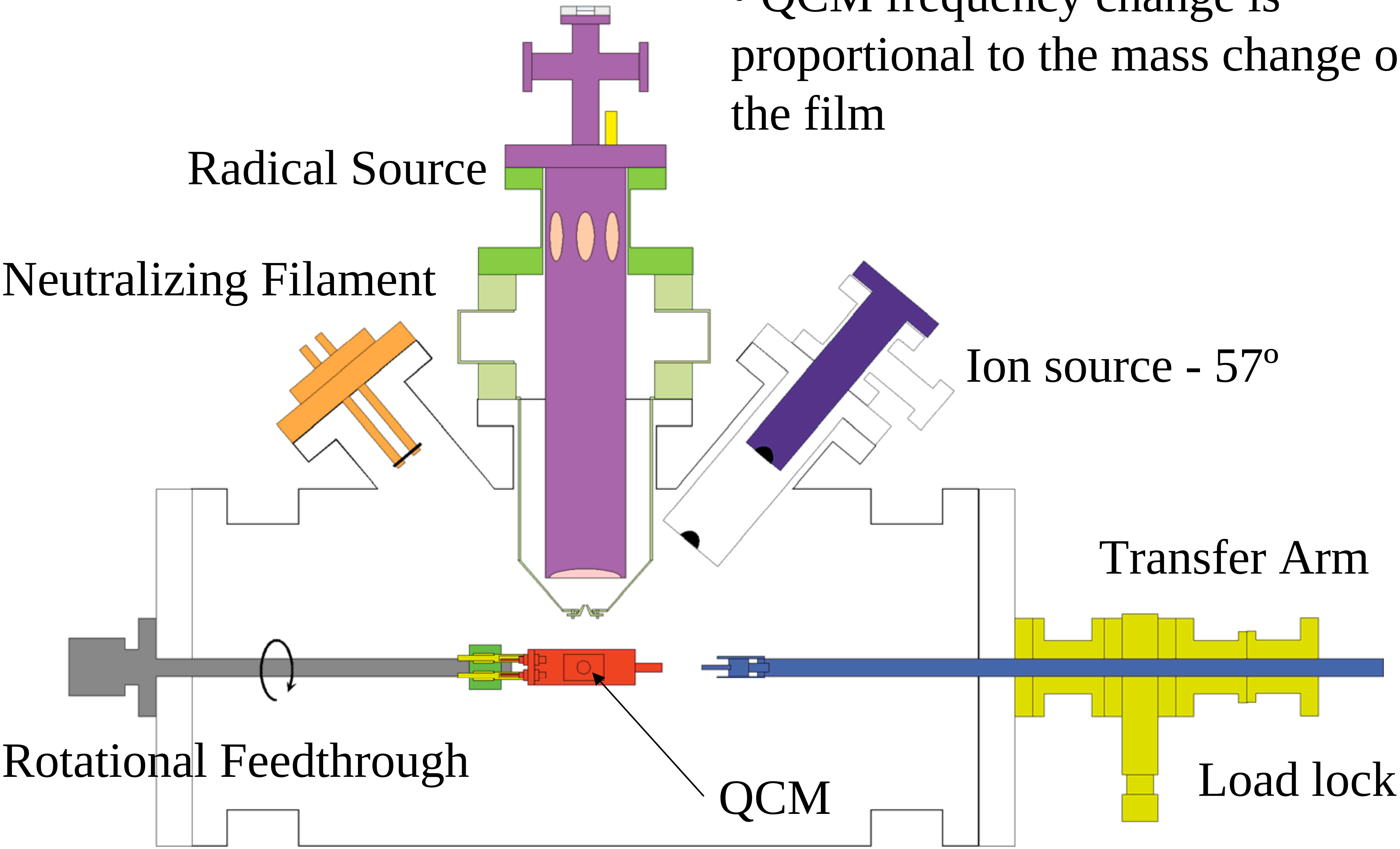
Determining Reflected/Desorbed Species



Sample is positioned in the exact previous location of the mass spectrometer!

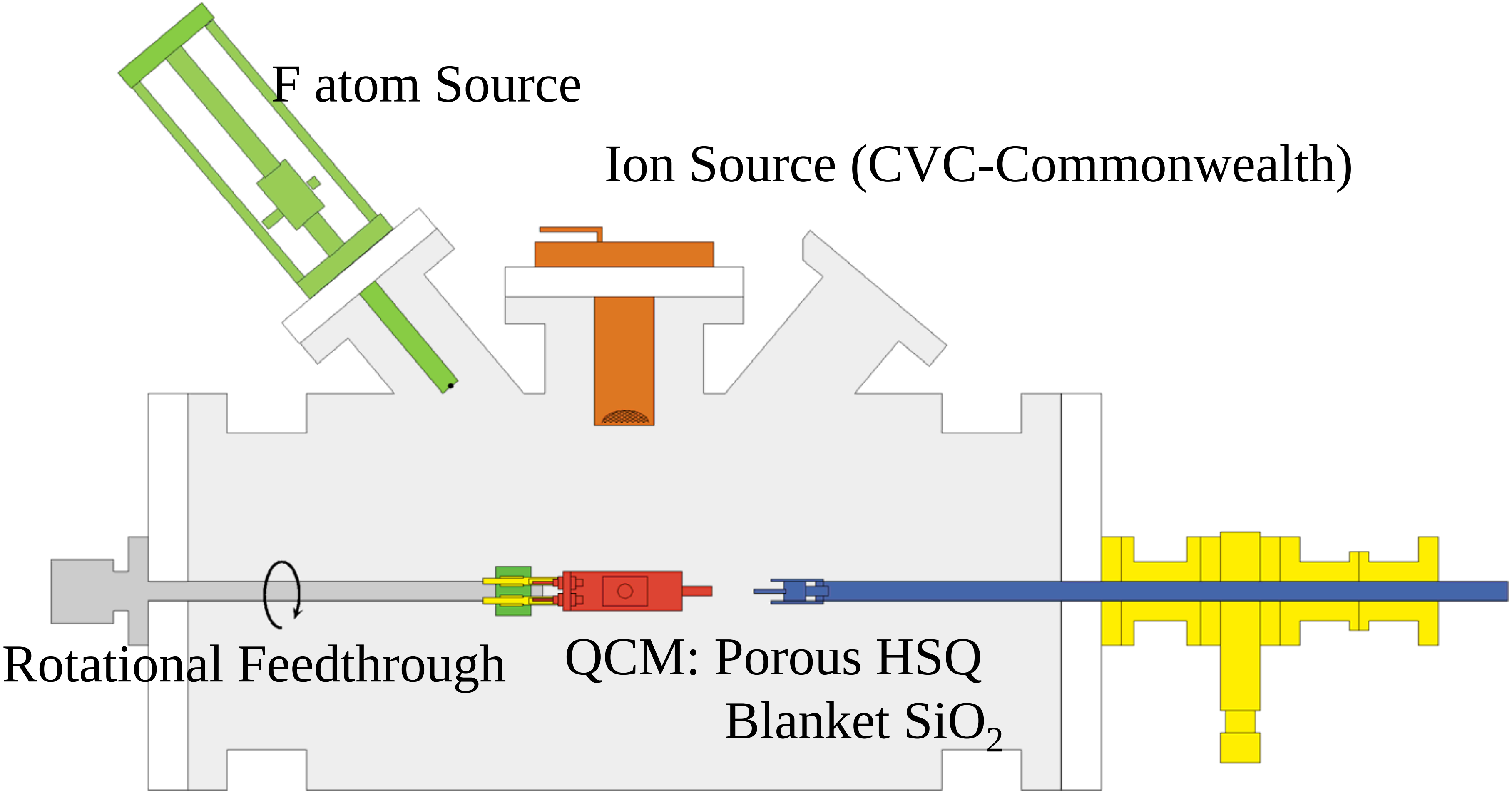
QCM Sample

• QCM frequency change is proportional to the mass change of the film



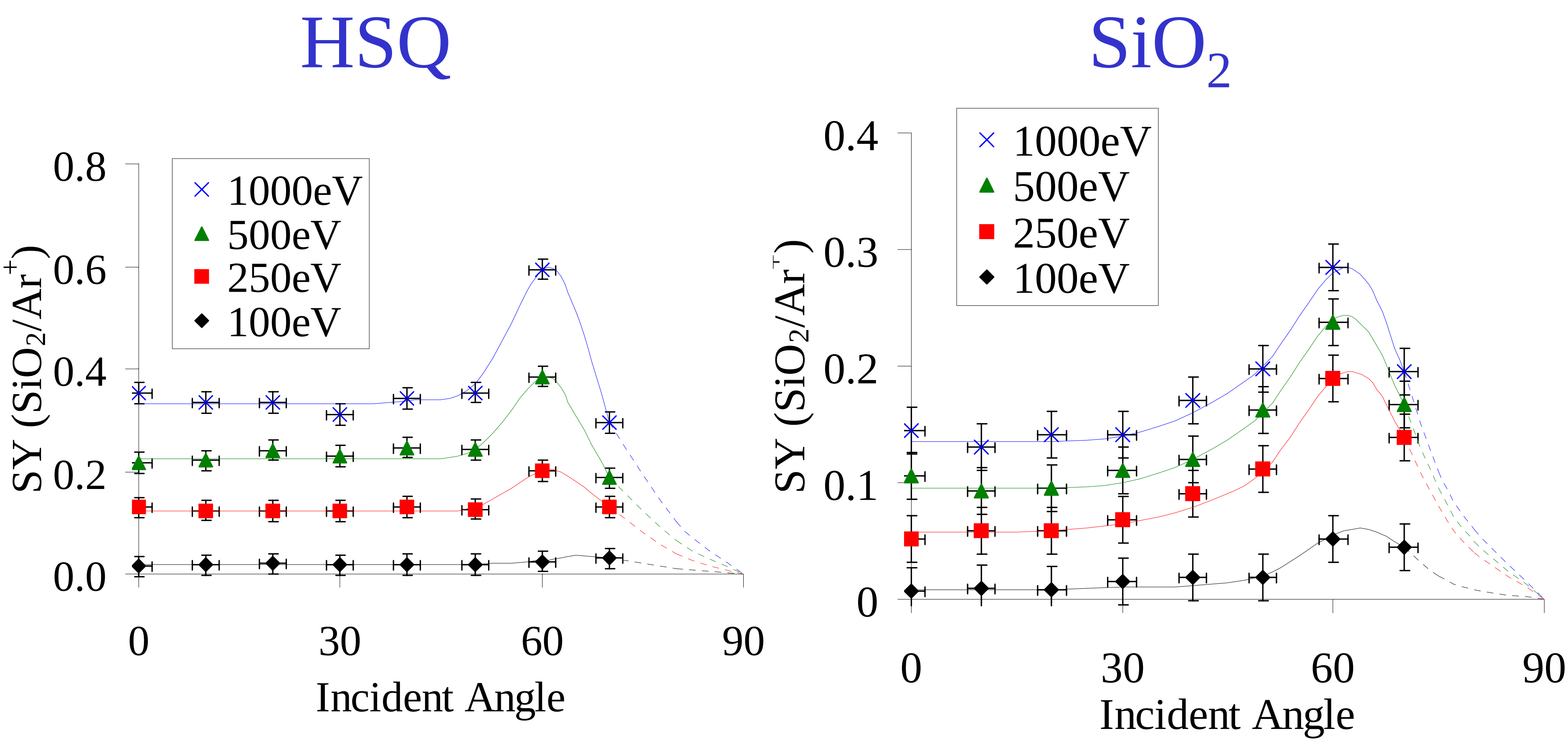
Studies with QCM: Porous HSQ

- Ar^+ incident angle effect on yield with and without F atoms
- Compared porous HSQ to blanket SiO_2



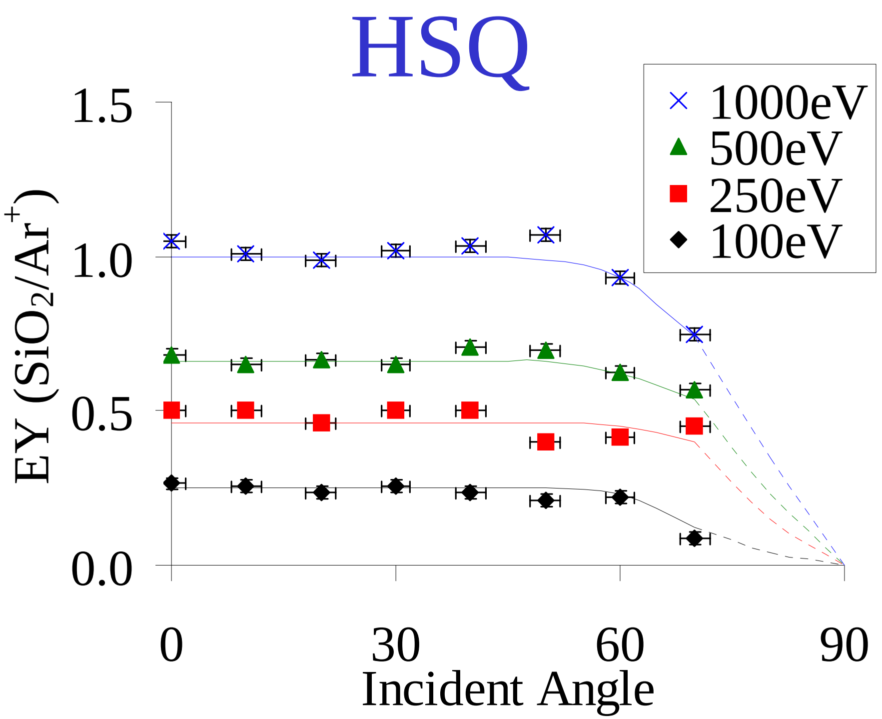
Studies with QCM: Ar^+ Sputtering

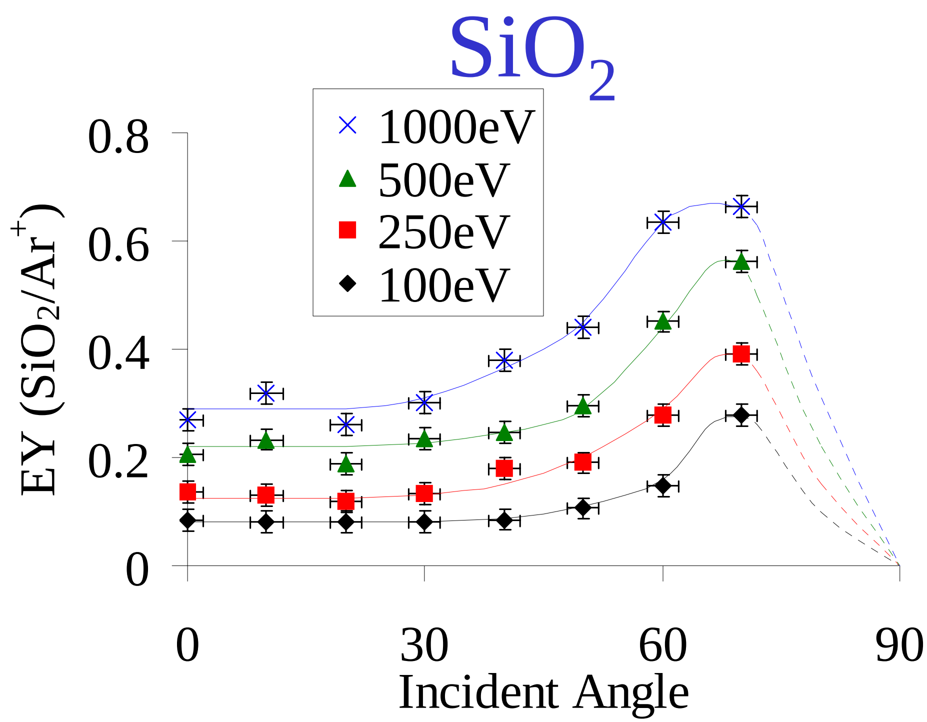
- Both exhibit a peak at 60°-70°
- The yield is higher for HSQ (~ 2x)
- Consistent with literature data for SiO_2



Studies with QCM: F and Ar^+ Etching

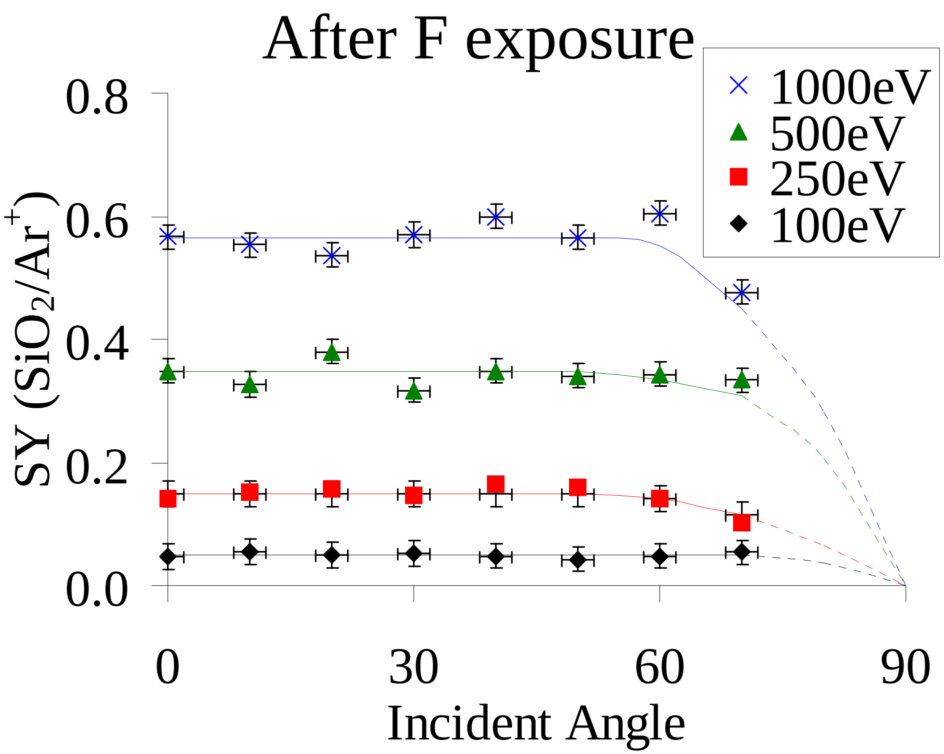
- HSQ angle dependence flattens near 60°-70°
- SiO_2 yield increases but angle dependence similar
- The yield is significantly higher (~ 3x) for HSQ

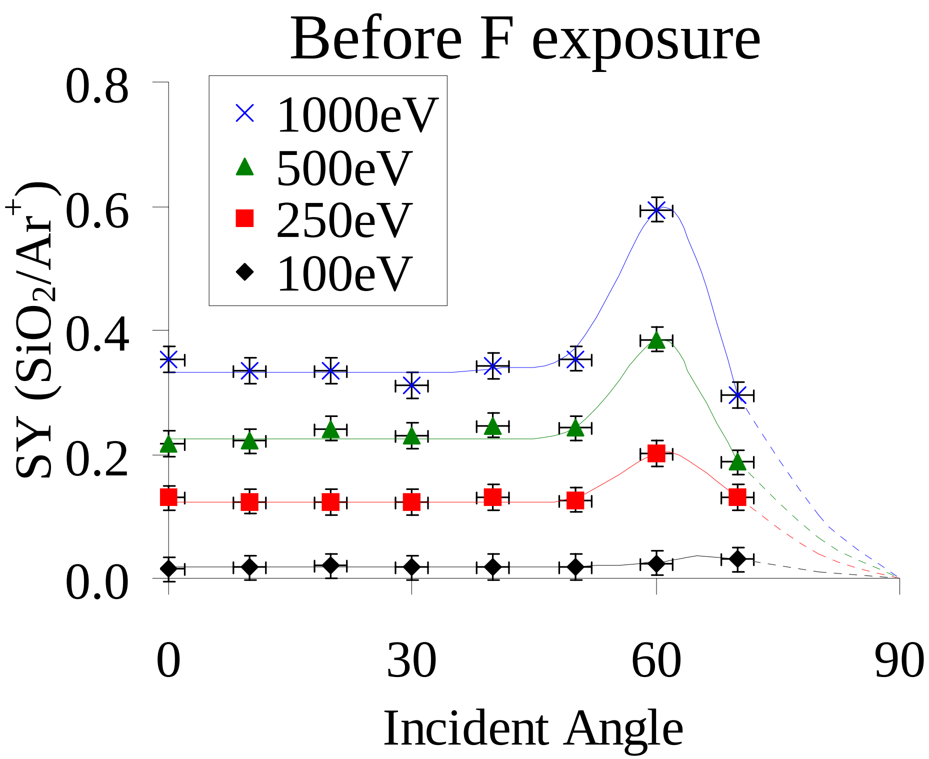




Studies with QCM: Ar^+ Sputtering after F atom exposure for HSQ

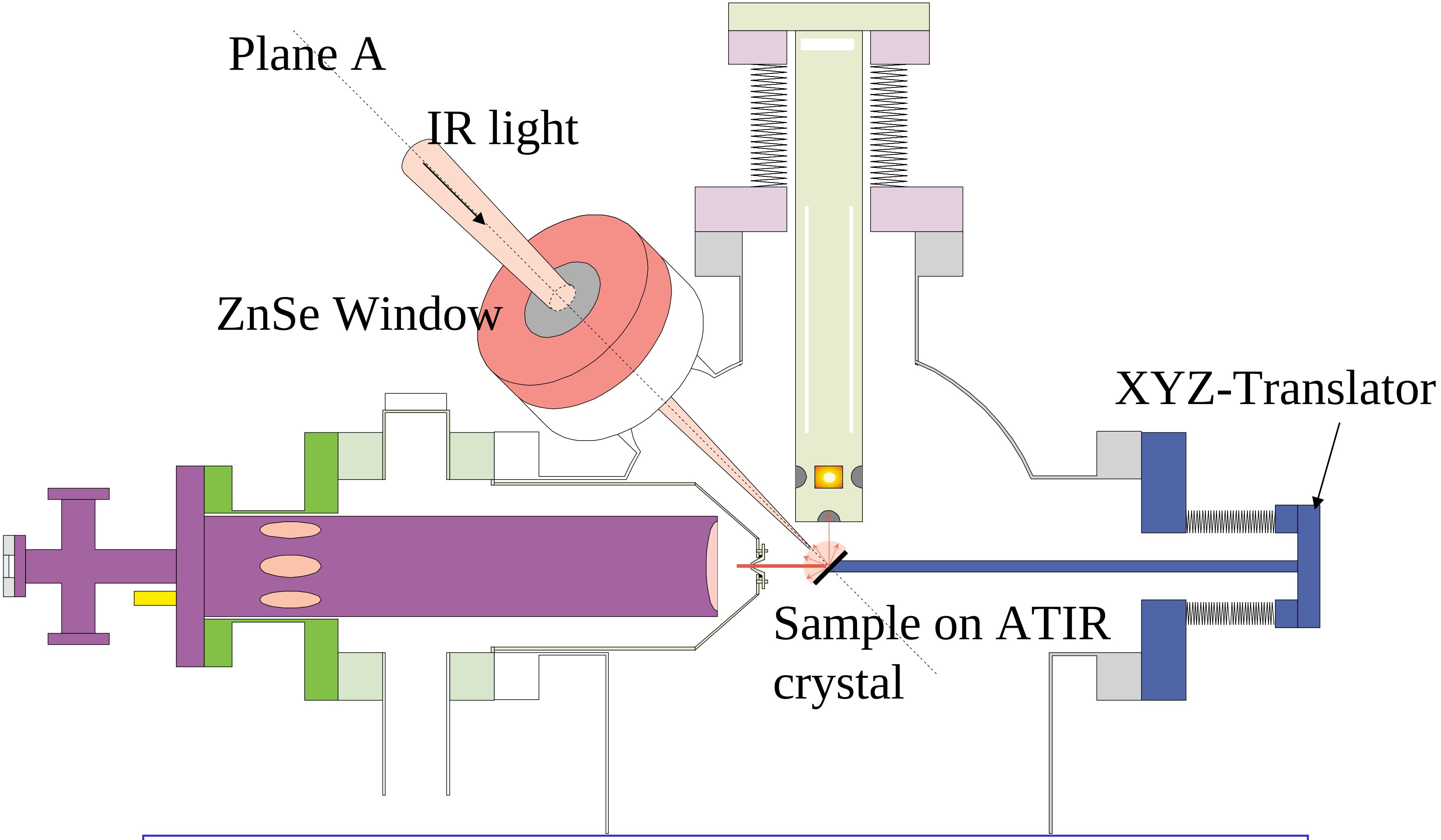
- After F exposure, HSQ loses the peak at ~60°
- Yield higher after F exposure, but not as high as simultaneous exposure
- Enhanced rate after F exposure persists for ~ 400 nm (film thickness)
- ***Suggests significant F uptake by pores throughout HSQ***



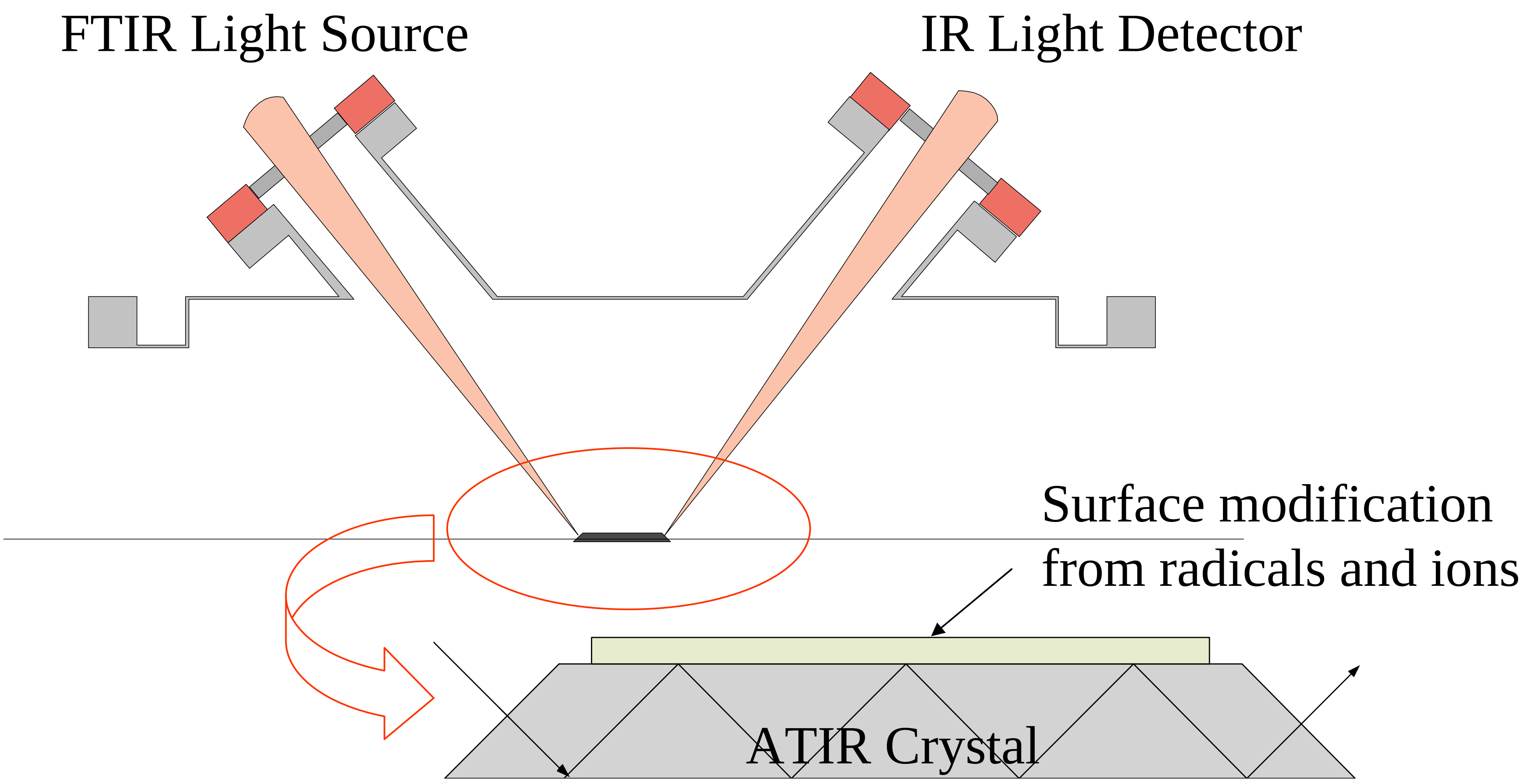


ATIR-FTIR Setup

- Detecting surface functional groups due to radical and ion fluxes

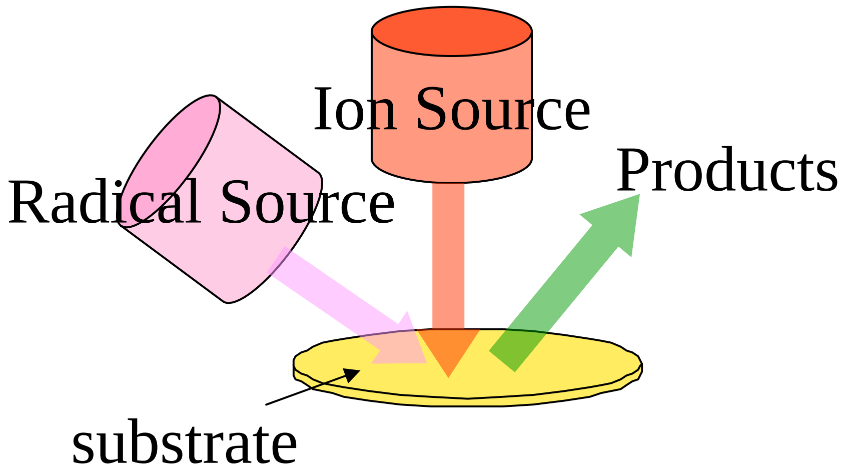


ATIR-FTIR Setup: Plane A



Detect surface functional group changes *in situ* during radical and ion exposure by detecting light absorption differences

Vacuum Beam System



TIMS for radical fluxes

- QCM for *in situ* etch/deposition rate determination
- ATIR-FTIR for *in situ* surface function groups
- TIMS to detect reflected and desorbed species from the surface

Example Study: C_xF_y Films Exposure to O and NH_3

• O atoms play a key role during ashing to remove any C_xF_y residual film on via walls

• If C_xF_y residual film remain after ashing, the film would be exposed to precursor for barrier deposition such as NH_3

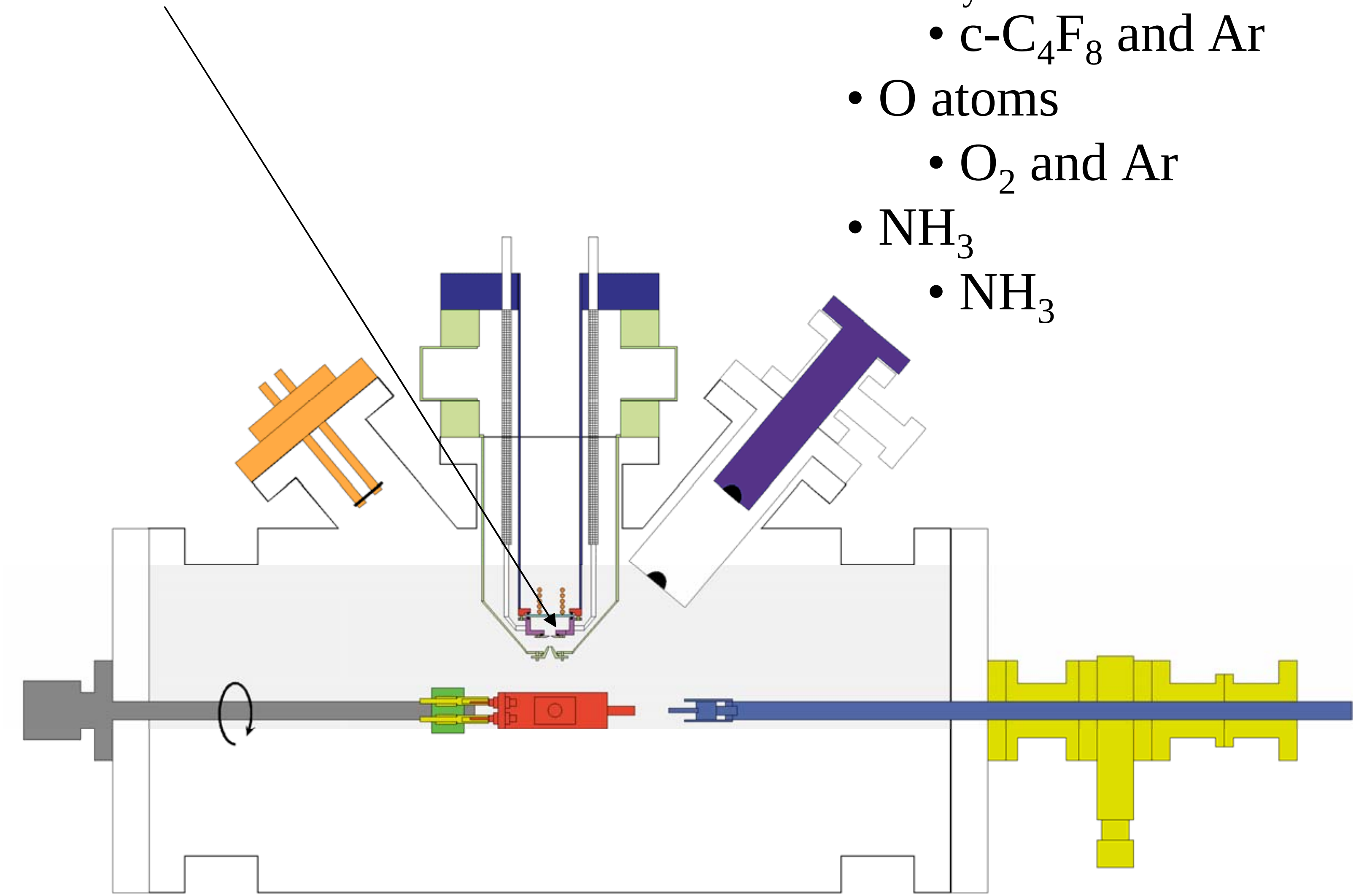
How do O atoms and NH_3 affect residual C_xF_y films?

- Deposited two types of C_xF_y films on QCM and ATIR crystals
- Observed etch/deposition rates during O and NH_3 exposure
- Observed products from the surface reactions
- Observed functional changes due to NH_3 exposure

Example Study: System Overview

Homemade plasma radical source:

- C_xF_y radicals/stable species
  - c-C_4F_8 and Ar
- O atoms
  - O_2 and Ar
- NH_3
  - NH_3



TIMS: C_xF_y Films Deposition

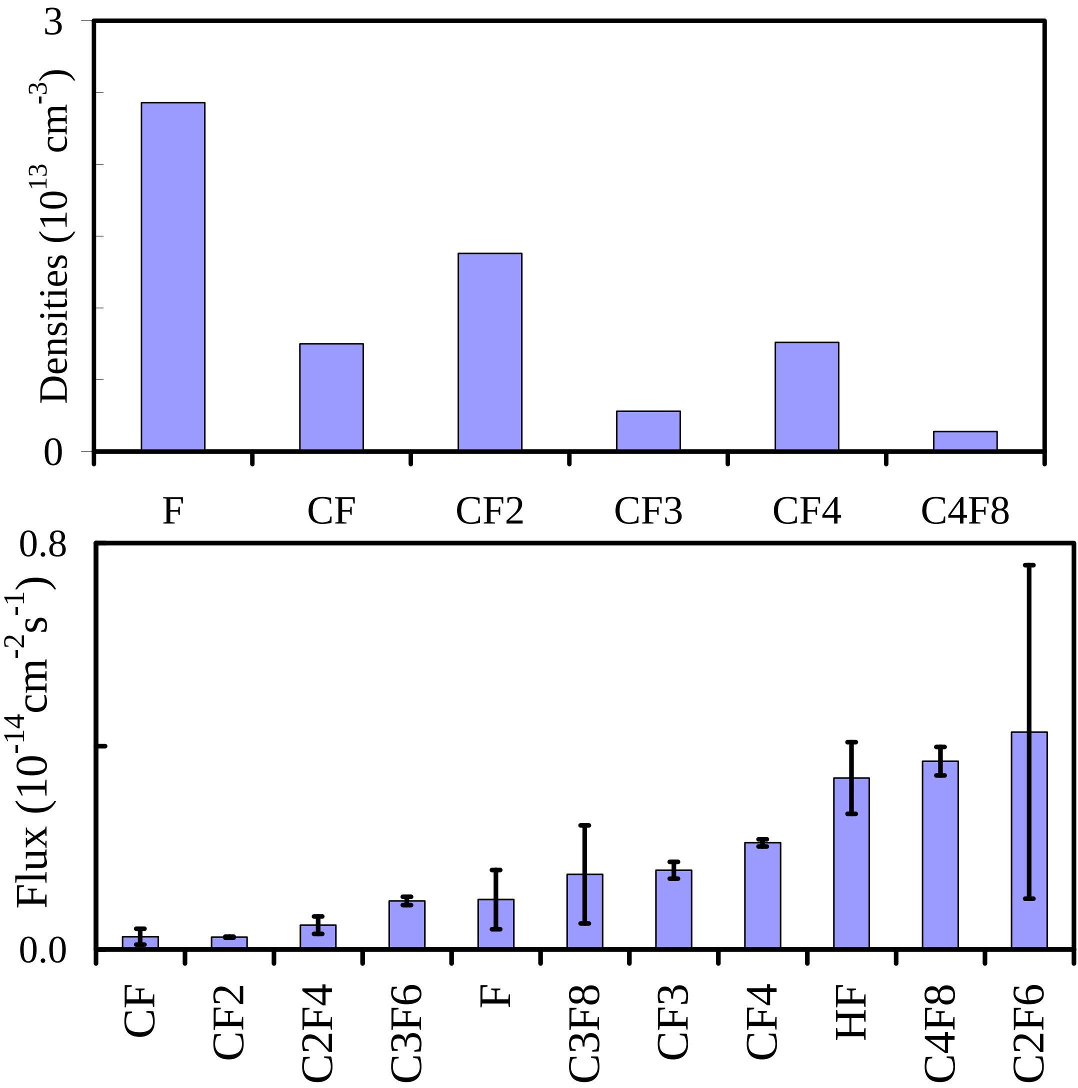
Deposited 2 types of C_xF_y films with c-C_4F_8 and Ar plasma

• Commercial scale ICP chamber [3]

QCM: ~150 CF_2 monolayers

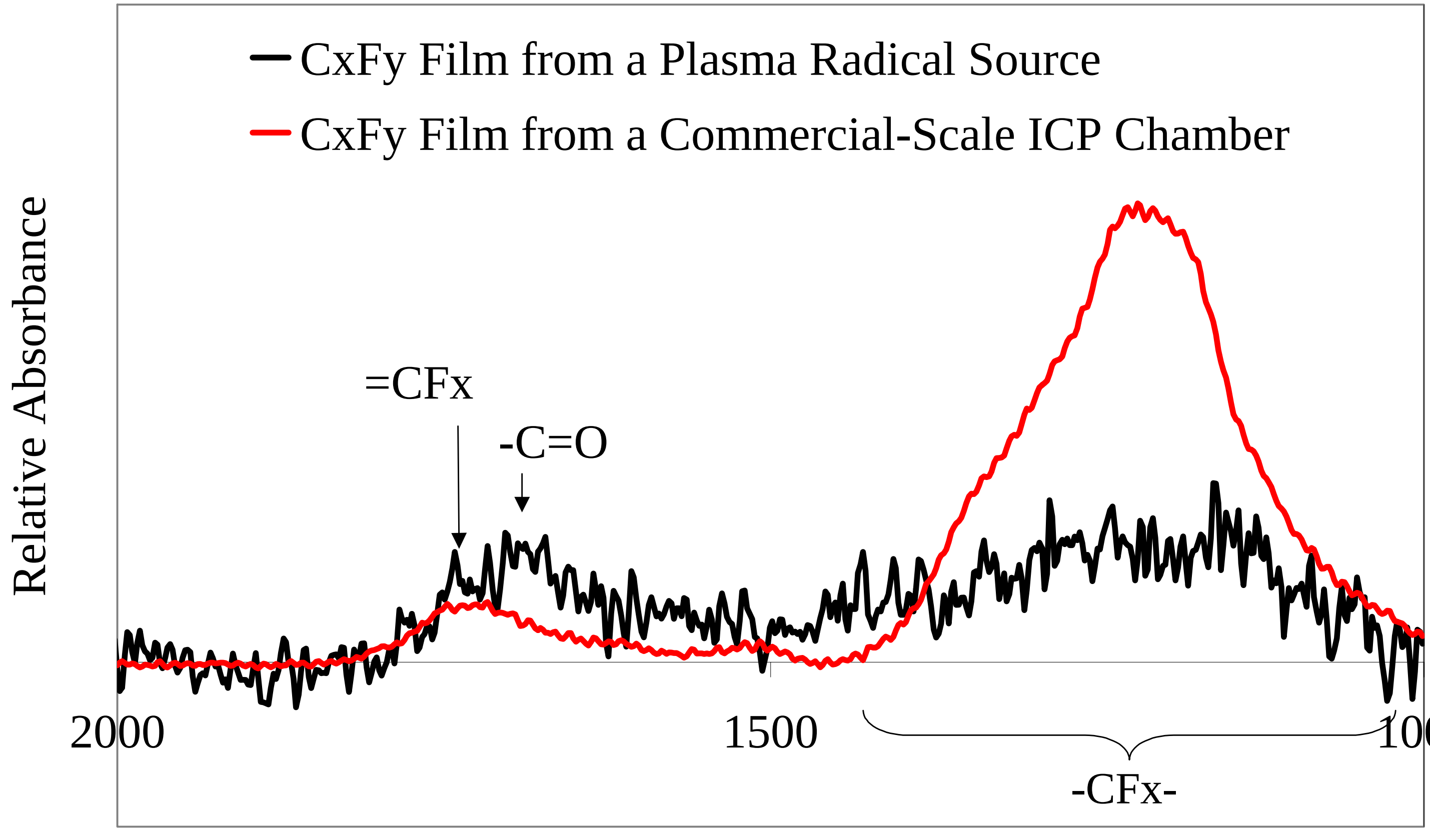
• Homemade plasma radical source used on the vacuum beam system

QCM: ~50 CF_2 monolayers



3 Hsu, J.

ATIR-FTIR: C_xF_y Films



- C_xF_y film from plasma radical source contains oxygen in the film

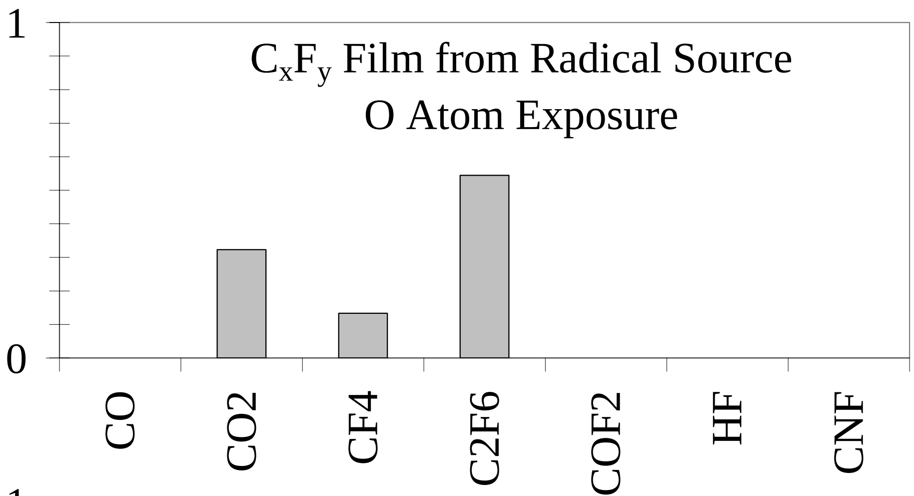
QCM: Etch/Deposition of C_xF_y Films

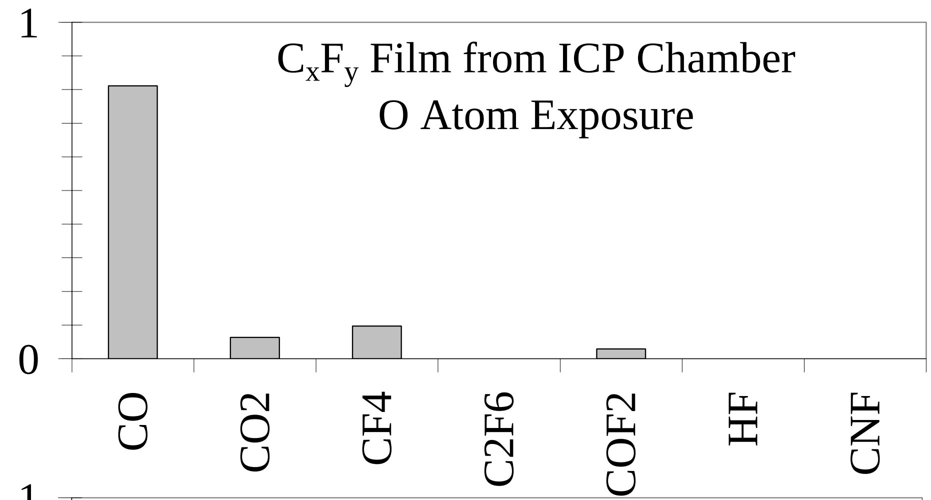
C_xF_y Film	Flux of O or NH_3	Etch Rate ($CF_2/cm^2/s$)
Radical Source	4.6×10^{14} $O/cm^2/s$	3.1×10^{12}
ICP Chamber	7.0×10^{13} $O/cm^2/s$	1.9×10^{11}
Radical Source	6.7×10^{13} $NH_3/cm^2/s$	6.7×10^{11}
ICP Chamber	6.7×10^{13} $NH_3/cm^2/s$	-1.4×10^{11}

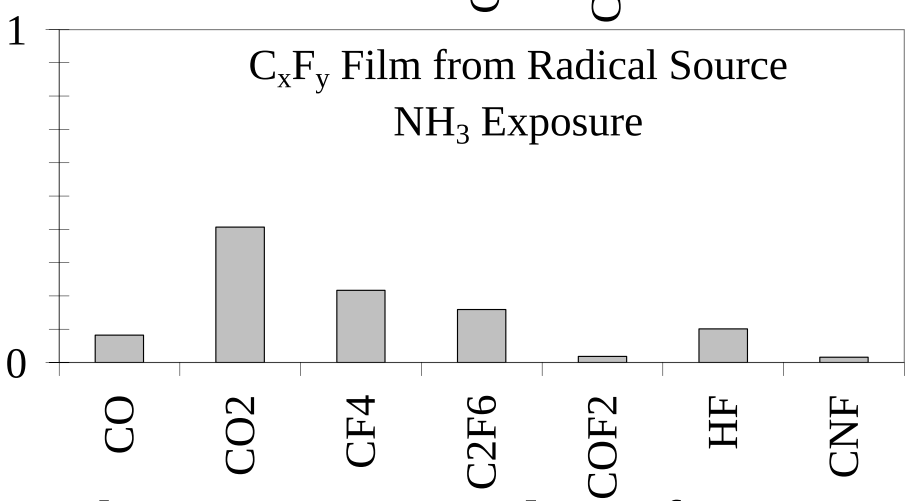
Low reaction probability: $< 1\%$

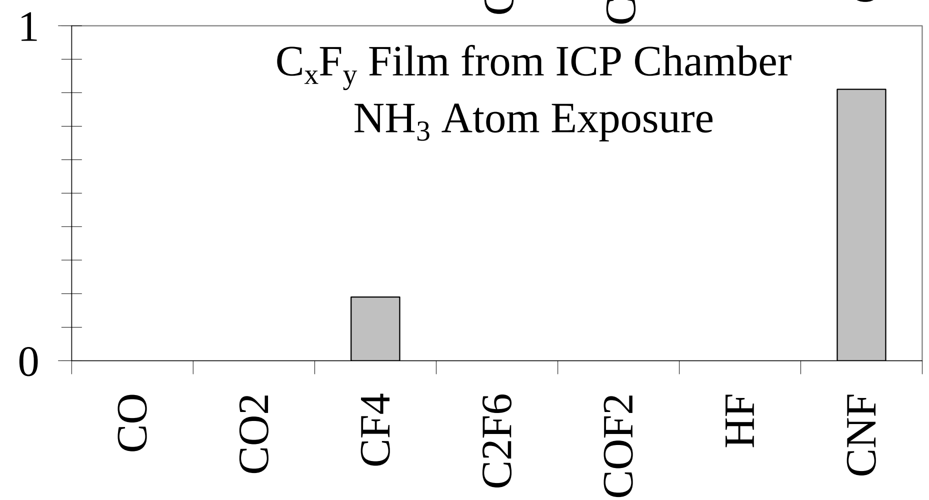
Deposition for NH_3 for film deposited in ICP chamber

TIMS: Product Distribution





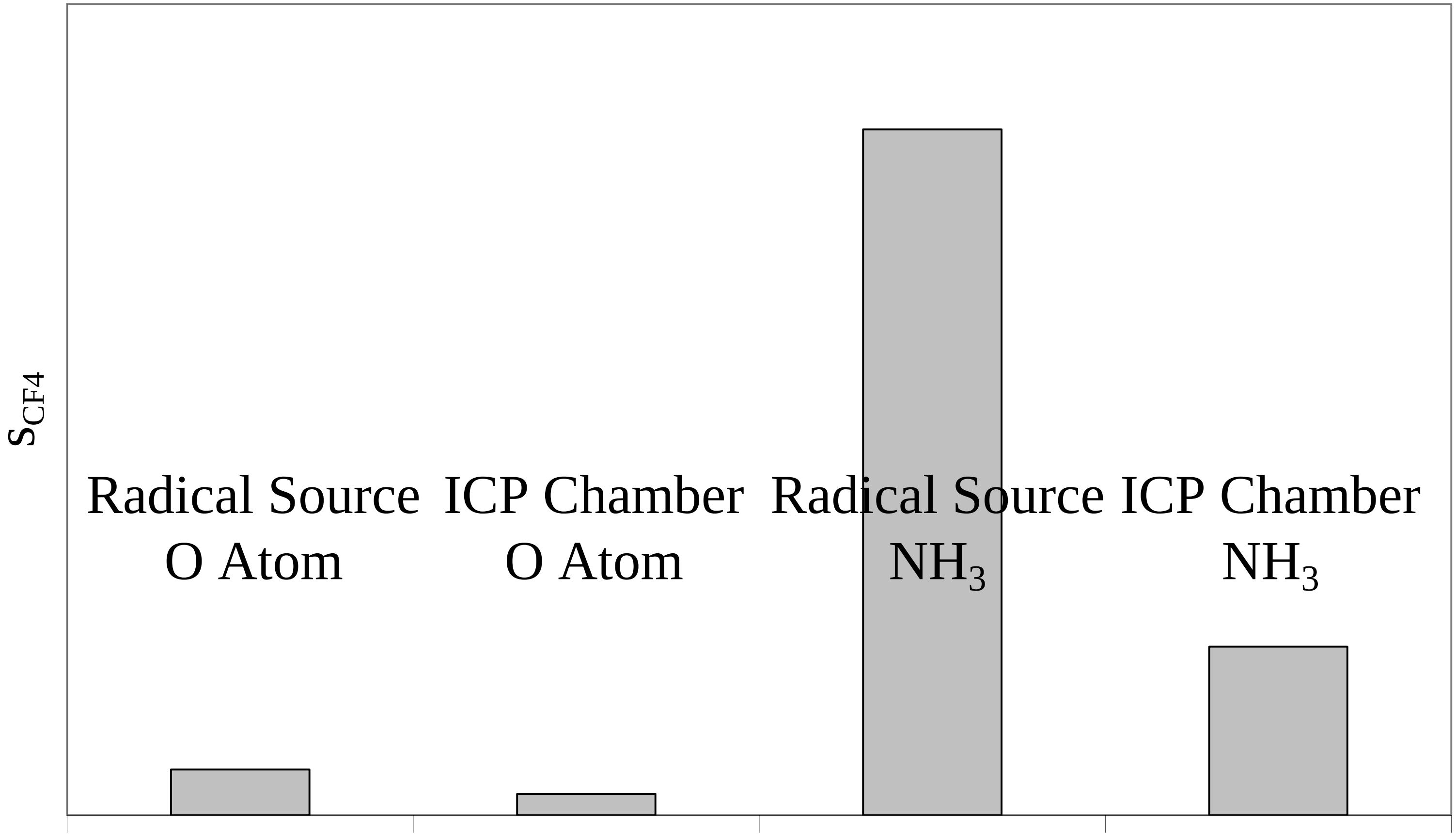




- Observe CNF products for NH_3 exposure
- Observe products during NH_3 exposure on C_xF_y from ICP Chamber

Net QCM rate is the result of NH_3 deposition and product desorption

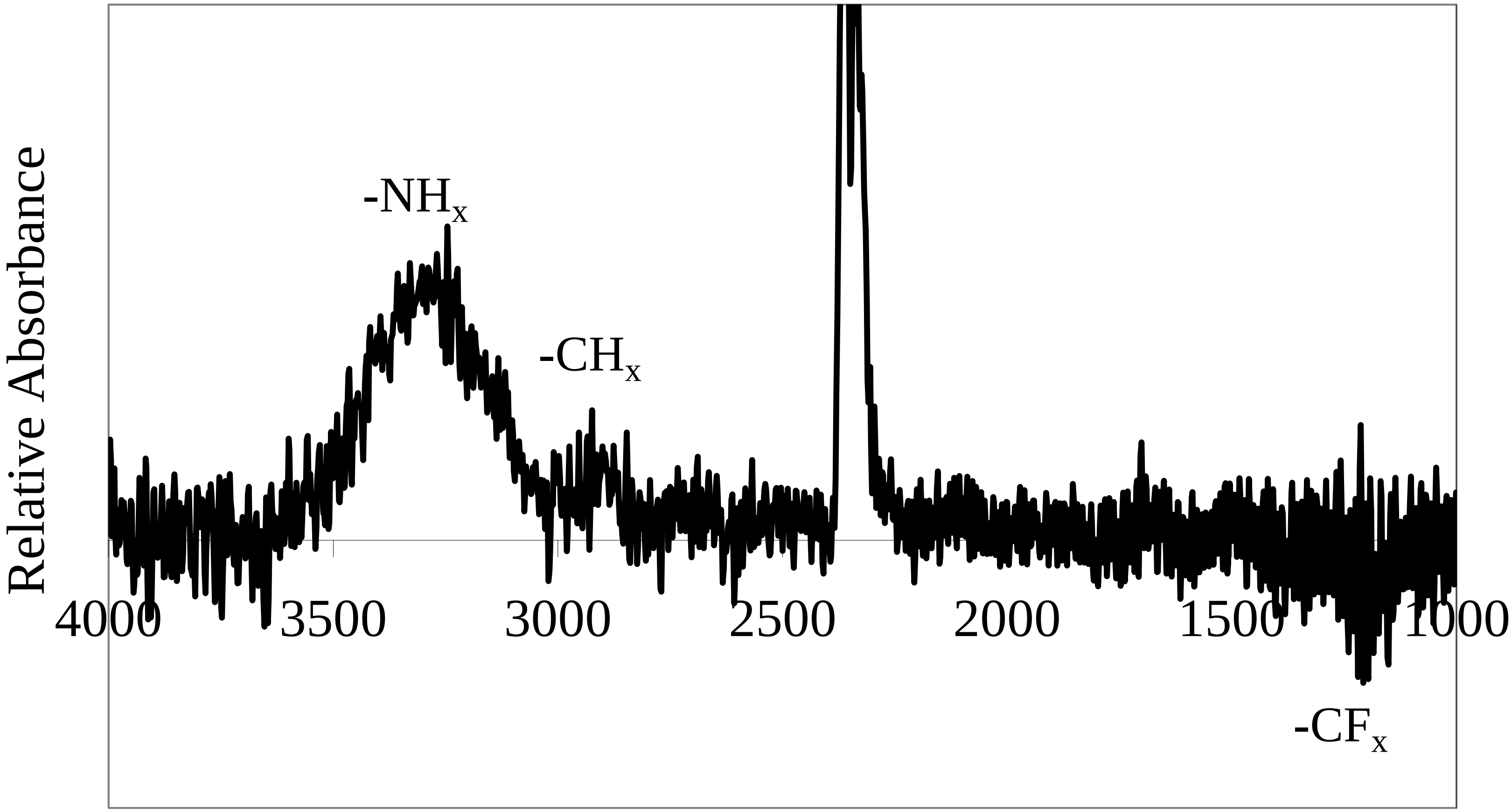
TIMS: CF_4 Signal



- CF_4 signal is much large for NH_3 exposure than for O exposure

Net QCM rate observed is the difference between *large* NH_3 deposition and *large* product desorption flux

ATIR-FTIR: NH_3 Exposure



- Large increase in $-NH_x$ signal
- Small increase in $-CH_x$ signal
- Decrease in $-CF_x$ signal

- NH_3 is highly reactive on C_xF_y films
- Changing the film from C:F to C:N:H

Example Study: C_xF_y Films Exposure to O and NH_3

- O atoms react at less than 1% probability:
  - QCM detection

- NH_3 is highly reactive
  - TIMS signal of CF_4
  - ATIR-FTIR detection of $-NH_x$

- NH_3 modifies the C_xF_y film into a film with C, N, and H
  - TIMS product distribution
  - ATIR-FTIR increased detection of $-NH_x$ and $-CH_x$ and decrease detection of $–CF_x$
  - QCM net mass change rate

Concluding Remarks

Vacuum Beam System

TIMS for radical flux characterization

QCM for *in situ* etch/deposition rate determination

ATIR-FTIR *in situ* surface functional change detection

TIMS for product/reflected flux characterizaiton

- QCM study of F and Ar^+ etching of porous HSQ
  - F contamination in the pores

- System study of O and NH_3 exposure on C_xF_y films

System designed to reveal fundamental radical-surface and ion-surface interactions